PHOTO-ELECTRIC CELLS AND THEIR APPLICATION — ANDERSON

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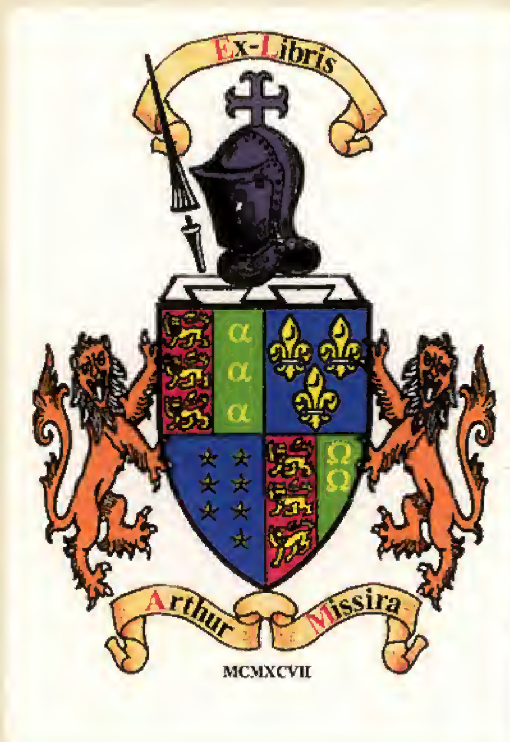

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PHOTO-ELECTRIC CELLS & THEIR APPLICATIONS

A DISCUSSION AT
A JOINT MEETING OF THE PHYSICAL
AND OPTICAL SOCIETIES
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EDITOR
JOHN S. ANDERSON
M.A., D.Sc., F.Inst.P.

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THE EARLY HISTORY OF PHOTO-ELECTRIC AND SELENIUM CELLS

By Professor H. S. ALLEN, M.A., D.Sc., F.R.S.,
University of St Andrews.

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ABSTRACT. A brief account is given of the discovery of photo-electricity and of the laws obeyed in the emission of photo-electrons. The early attempts to employ photo-electric cells in photometry are described and the main types of cell are indicated. Two actions of light on selenium are described—(1) the change in resistance discovered by Willoughby Smith and May, (2) the production of an electromotive force when selenium is used as an electrode in an electrolytic cell.

§ 1. INTRODUCTION

IF we assume with Kelvin that accuracy of measurement is an index of the state of development of any branch of science, it is evident that measurement of quantity of light is a matter of great importance in a civilised community. The human eye, when used in making a direct estimate of light, affords only a rough indication of intensity, and, although it is fairly sensitive in judging equality of brightness, it is sometimes desirable in photometry to avoid the personal characteristics of the observer's vision by employing apparatus which will give more consistent and, perhaps, more accurate results. Two such pieces of apparatus, the photo-electric cell and the selenium cell, are to be the subject of the present discussion. Both depend upon an electrical change brought about by the action of light, and both might be included under the general title of photo-electric devices. But it is convenient to use the term "photo-electric" cell to describe an apparatus in which the effect due to the light is the production of an electron current which is made the subject of measurement, while in the selenium cell the effect measured is (usually) the change in electrical resistance of the illuminated material. In this paper it is proposed to give a short historical survey of the development of these two types of detector.

§ 2. PHOTO-ELECTRICITY

In the experiments of Hertz (1887) on the effects of resonance between very rapid electric oscillations it was noticed that an electric spark took place more readily when the spark gap was exposed to another spark than when it was screened in a dark case. This action was traced to an effect of ultra-violet light upon the spark discharge. Hertz concluded that ultra-violet light has the property of increasing the sparking distance of the discharge of an induction-coil, and of other discharges. The simplest effect was obtained with the glow-discharge from 1000 small accumulators

between brass knobs in free air; by the action of light the glow-discharge could pass when the knobs were so far apart that it could not spring across without the aid of the light.

In 1888 simpler means of studying the effect were employed by Hallwachs, who examined the action of light from an electric arc or from burning magnesium ribbon on a charged body placed in connexion with a gold-leaf electroscope. Hallwachs observed that a polished metal plate, which has been insulated and given a negative charge, loses that charge on exposure to ultra-violet light; but when it is given a positive charge, practically no effect is produced by the light. It was also shown that an insulated body, originally uncharged, acquires a positive potential when exposed to ultra-violet light. In 1889 Elster and Geitel, who were very active in investigations on all types of electrical change, found that the electro-positive metals, sodium, potassium, and rubidium, were affected in a similar way when exposed to ordinary light. The same experimenters made the important discovery that at low pressures the photo-electric current is diminished by a transverse magnetic field, an observation which afforded a method of measuring the ratio of the charge to the mass of the particle responsible for the change in electrification. Subsequently J. J. Thomson proved that this charge was the same in value as the elementary charge carried by the hydrogen ion in electrolysis, which is in fact the "electron" charge of Johnston Stoney.

For the elucidation of the phenomenon of photo-electric emission it is necessary to carry out experiments in a very high vacuum, and it was shown independently by J. J. Thomson and by Lenard that in this case the current is carried by "corpuscles" or "electrons." By methods of experimenting, simple in theory but somewhat difficult in practice, it is possible to measure the number of electrons leaving the illuminated plate, and also the velocity—in particular the maximum velocity—with which they leave the plate. The results of such experiments show that within a wide range of temperature both the number of electrons emitted and the velocity are independent of temperature. This remarkable fact has only recently been fully explained. It seems that most of the electrons in a metal have an energy independent of temperature, and this energy is nearly the same for all these electrons. The photo-electrons, as we may term the electrons emitted under the influence of light, are derived from this class. Two of the most important facts of photo-electricity are those concerned with changes in the intensity of the light, due either to altering the distance between the source and the receiver or to the interposition of rotating sectors. It is found that the velocity of the electrons is independent of the intensity of the light, whilst the number of electrons is directly proportional to the intensity over a very wide range. It is this last fact which is of fundamental importance in connexion with photo-electric photometry.

The influence of the wave-length of the exciting light on the photo-electric activity is a question of great theoretical interest and of considerable practical importance. In general—at least in the so-called "selective" effect when the electric vector in the light is parallel to the plane of incidence—the number of electrons emitted reaches a maximum value for a particular wave-length, usually in the visible part of the spectrum.

As regards the relation between the velocity of the electrons and the wave-length or frequency of the exciting light, there is clear experimental evidence that the maximum energy of emission is a linear function of the frequency of the light. This result is in agreement with the formula suggested in 1905 by Einstein on the hypothesis of the existence of light-quanta. For each metal there is a certain characteristic or "threshold" frequency, which determines the photo-electric behaviour, and also (when multiplied by Planck's constant, h) the "electron affinity" or "work function," i.e. the amount of work done when the electron escapes from the atom to which it is attached. To illustrate Einstein's equation let us consider the metal potassium, frequently used in photo-electric cells. For the normal metal which has not been sensitised the threshold is close to 7000 Å.U., corresponding to a characteristic frequency of about $4{\cdot}3 \times 10^{14}\ \text{sec}^{-1}$. Einstein's equation implies that if the light is slightly redder than this it may fall on potassium for centuries without causing the emission of electrons, but if the light has greater frequency it will at once bring about the liberation of electrons and the velocity (or, more strictly speaking, the kinetic energy) of emission will increase as the frequency increases. The maximum energy of emission is directly proportional to the difference between the frequency of the exciting light and the characteristic frequency, and the factor of proportionality is Planck's constant. In fact Einstein's equation provides one of the most accurate methods of determining this important constant.

§ 3. PHOTO-ELECTRIC CELLS

The use of a photo-electric cell for photometry was suggested by Hallwachs, who had found that the photo-electric activity of copper oxide (CuO) was constant over long periods of time. Such a cell was employed by his pupil R. Lindeman in an investigation of the radiation from an arc lamp.

Elster and Geitel had already made measurements of the ultra-violet light in the sun's rays with the aid of a freshly amalgamated sphere of zinc connected to an electroscope. The discovery which they had made in 1889 that the alkali metals were sensitive to ordinary light was the starting point of an important development. Harms in 1906 used one of Elster and Geitel's alkali cells, as did Bergwitz in 1907, and four years later he used an improved cell of the latest construction for the photo-electric measurement of sunlight in the course of a balloon ascent. Elster and Geitel continued their work on potassium cells and in 1912 made a determination of the smallest amount of visible light capable of producing a measurable electron current. The minimum luminous energy discoverable from a Hefner lamp, using a single-fibre electrometer to measure the current, was of the order 10^{-7} erg./sec. cm.^{2}.

To secure a photo-electric cell suitable for visible light the potassium surface was sensitised by passing a glow discharge through hydrogen gas, and an argon or helium atmosphere was substituted for hydrogen. Their photometer, which resembled a small gun and was mounted like a theodolite, was used at Wolfenbüttel during the total eclipse of April 17, 1912. For field work a dry battery of 40 volts and a galvanometer giving one division per microampere was employed, but in the laboratory an electrometer was used and currents down to 10^{-12} ampere measured.

The modification produced by "sensitising" the potassium surface is not as yet clearly understood. It has been regarded as the formation of a hydride of potassium and of a colloidal layer. But, according to Campbell and Ritchie, it is more probable that part of the change is optical and part the formation of a surface layer of hydrogen. Whatever may be the nature of the process, the result of sensitising is to increase the activity and to shift the maximum effect and also the threshold towards the region of longer wave-lengths.

Photo-electric cells containing alkali metals may be divided into two types. In the first type the sensitive metal is distilled on a coating of silver previously deposited on the glass wall of the cell. In the second type the alkali metal is distilled upon a metal plate in the interior of the cell.

Another way of classifying the cells is to distinguish between "vacuum" cells and "gas-filled" cells. In the former type the vacuum is supposed to be so high that a pure electron discharge passes when the sensitive surface is illuminated. In the latter type the cell contains a certain amount of one of the inert gases, or a mixture of such gases, and the current is amplified within the cell by employing an electric field strong enough to produce ionisation by collision.

W. W. Coblentz, who carried out a series of investigations for the Bureau of Standards on instruments and methods used in radiometry, thus summarises (in 1918) the properties of the photo-electric cell. "The distinguishing characteristic of the photo-electric cell is its selective sensitivity to various wave-lengths, being the most sensitive to the ultra-violet. Thus far it has not been possible to modify appreciably this inequality of sensitivity for different parts of the spectrum. However, while most photo-electric cells do not give responses which are directly proportional to the intensity of the incident radiation, it is possible to design the cell so that it gives direct proportionality of response."

§ 4. SELENIUM "CELLS"

The discovery that selenium changes its resistance under the influence of light was due to Willoughby Smith and his assistant May in 1873*. The former began experiments on selenium with a view to obtaining a high resistance suitable for use with submarine cables. In the course of these experiments remarkable fluctuations in resistance were observed. "It was on the 12th of February, 1873, that the Society of Telegraph Engineers received a communication from Mr Willoughby Smith, one of its members, of an observation made first by Mr May, a telegraph clerk at Valentia. A stick of crystalline selenium offered considerably less resistance to a battery current when exposed to the light than when kept in the dark."

Selenium exists in two forms: the vitreous form, which is a non-conductor of electricity, and the granular or crystalline form, which conducts electricity at ordinary temperatures. The conductivity of the crystalline form is increased by exposure to light, especially to yellow and red light, and to a smaller extent by exposure to infra-red rays. In very bright sunlight the conductivity may be increased tenfold or more. The response to the action of light takes place fairly rapidly, a fact utilised by

* *Journn. Soc. Tel. Eng.* **2**, 31 (1873).

Graham Bell in 1880 in the construction of the "photophone," by means of which articulate speech could be transmitted along a beam of light.

There is a second action of light on selenium which may be employed in photometry. Sabine in 1878 showed that an electromotive force is generated when selenium, used as an electrode in a voltaic cell, is exposed to light. This arrangement was used by Minchin (1895–6) in the photometry of stars, and he obtained an electromotive force of 0·03 volt by illuminating a sensitive surface of 0·645 sq. cm. by means of a candle at a distance of 274 cm. Minchin pointed out that it would be strictly correct to speak of such an electrolytic cell as a selenium "cell," but those "cells" in which the action due to light is a change in the resistance of selenium might more properly be termed selenium "bridges."

The efficiency of selenium as a detector of light was investigated in 1913 by Fournier d'Albe, who devoted special attention to the limits up to which minute quantities of light and minute variations of its intensity may be discovered. In an experiment described by Fournier d'Albe, an illumination of 10 microlux was obtained by making a minute hole in tinfoil, and the current was 0·0222 microampere. Elster and Geitel, using a potassium photo-electric cell, observed a current of $6{\cdot}7 \times 10^{-14}$ ampere when the illumination received was 3 microlux. "Selenium, therefore, with the same illumination and extent of sensitive surface, is capable of giving a measurable effect at least 100,000 times greater than that furnished by a potassium photo-electric cell."

The faintest star clearly visible to the naked eye is usually assumed to be of the sixth magnitude. Fournier d'Albe estimates that the limit of human vision corresponds to an illumination of 3 milli-microlux, and, assuming the diameter of the pupil in the dark to be about 6 mm., the minimum flux of light perceptible to the eye is $8{\cdot}5 \times 10^{-14}$ lumen. The eye suffers in sensitiveness when the light is diffused; the selenium detector does not.

W. W. Coblentz (1918) reports that, although the selenium detector is extraordinarily sensitive to light, it has several objectionable characteristics which render it unsuitable for precise quantitative measurements of radiant energy. The sensitivity depends upon heat treatment and varies not only with the wave-length, but also with the intensity of the light stimulus. Further, it is slow in recovering its normal resistance after having been exposed to light. One of the principal disadvantages of the selenium detector is this "inertia," shown in the slowness with which the final conductivity is reached when the detector is illuminated, and the even greater slowness with which recovery takes place in the dark. The period of recovery increases with the intensity of the illumination to which the selenium has been exposed.

The law of light action for a selenium detector may be expressed by saying that, for a given period of recovery, the change of resistance is approximately proportional to the square root of the incident energy.

A THEORY OF SELECTIVE PHOTO-ELECTRIC EMISSION

WITH SPECIAL REFERENCE TO THIN FILMS OF CAESIUM ON SILVER

By N. R. CAMPBELL.

(Communication from the Staff of the Research Laboratories of the General Electric Company Limited, Wembley.)

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ABSTRACT. An attempt is made to apply to photo-electric emission the conception of a transmission coefficient developed by Nordheim and Fowler in their application of wave-mechanics to thermionic emission. It appears that, if subsidiary assumptions of some plausibility are made, a satisfactory qualitative account can be given of normal photo-electric emission that involves no ideas that are not now firmly established.

The problem of selective emission is more difficult; it appears to require that the surface should transmit selectively electrons within a narrow range of velocity. In order to ascertain whether such a theory would be tenable, the problem is attacked in two halves. First, an attempt is made to discover what is common to all selectively emitting surfaces. It appears that the presence of an electronegative element is a universal feature; and it is suggested, on thermionic analogy, that this element forms a cement uniting a more electropositive layer (probably monatomic) on the outside to a massive but less electropositive metal on the inside. Support for this view is found in an examination of the formation of the cathodes of caesium on oxidised silver that have been described by Koller; this formation is described in detail.

Second, it is asked what surfaces might be expected to transmit selectively. A suggestion given by recent work of Fowler and Wilson, which is being developed by Fowler in a separate paper, indicates that, if the distribution of potential through the surface layer of the cathode were such as to form a potential "valley" between two potential "peaks," selective transmission would occur when the velocity of the electrons was such that the waves associated with them were capable of forming standing waves between the sides of the valley. A re-examination of the facts in the light of this suggestion leaves it possible that the constitution of selectively emitting cathodes may indeed satisfy this condition.

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§ 1. THE TRANSMISSION COEFFICIENT

It is now firmly established that the work function of a clean metallic surface determined from the thermionic emission is the same as that determined from the photo-electric threshold*. The conclusion is inevitable that the difference between thermionic and photo-electric emission lies only in the manner in which the electrons in the metal receive their energy, and that the circumstances deciding their emergence are precisely the same. The transmission coefficient $D(W)$, which measures the chance that an electron with energy W approaching the surface will

* See, for instance, L. A. Dubridge, *Phys. Rev.* **31**, 236 (1928).

pass through it, is the same whether that energy has been received from radiation or from molecular agitation; it is determined wholly by W and by the variations of potential occurring at the surface.

Although considerable knowledge of transmission coefficients has been derived from thermionic data, it is still not possible to calculate the photo-electric emission under given radiation in the same way as the thermionic emission at a given temperature can be calculated. For while the temperature, which determines the mean energy of the thermionic electrons, is constant throughout the metal, the radiation, which determines the energy of the photo-electric electrons, decreases rapidly within a distance from the surface which is comparable with the free path. The electrons are never in equilibrium with a constant field of radiation, but, since it is known that the absorption of the light does not vary very rapidly with the wave-length, some qualitative prediction can be made. $D(W)$ increases rapidly with W up to a maximum of 1 and, for the same number of quanta absorbed, the mean value of W must increase with the frequency. Hence the photo-electric emission per quantum absorbed should increase rapidly with the frequency, so rapidly in fact that the emission per unit of energy absorbed should also increase. This prediction is, of course, confirmed in the normal photo-electric effect for frequencies not too far from the threshold. At very much greater frequencies (e.g. X-ray frequencies) $D(W)$ has already reached its maximum and ceases to increase; the emission per unit of absorbed energy falls off, partly because the number of quanta in a given amount of energy decreases, partly more because the radiation is absorbed at greater distances from the surface.

Again Fowler* has shown that the theory is not inconsistent with experiments on the distribution of velocities among the emergent electrons: this distribution is certainly not Maxwellian, as is that of the thermionic electrons. But neither experiment nor theory gives sufficiently definite data for a complete test of the theory to be made.

§ 2. POLARISED LIGHT

Another feature of photo-electric emission which it seems possible to interpret in terms of the transmission coefficient is its dependence on the polarisation of the incident radiation. When the emission is normal and is reckoned on the basis of energy absorbed (and not of energy incident) there is generally no difference between P, the emission when the electric vector in the radiation is perpendicular to the surface, and L, the emission when the vector is parallel. Now it is certain that the momentum that the electrons acquire when they take up energy from radiation tends to be in the direction of the electric vector; if it were not, there would be no polarisation of X-rays, or indeed any kind of polarisation detectable experimentally. On the other hand, the energy W, which determines $D(W)$, is the energy associated with the component of the momentum perpendicular to the surface; $D(W)$ increases rapidly with W, and hence we should expect $D(W)$ to be greater, for equal energy received, when the momentum received is perpendicular to the surface; that is to say, we should expect P to be greater than L. Actually when the emission is from

* R. H. Fowler, *Proc. R. S* **118**, 229 (1928).

clean metal surfaces, they are nearly equal. Now Nordheim's work* shows that, for such clean surfaces, $D(W)$ is of the order of 1, even when the energy but slightly exceeds the work function; on the other hand, the number of electrons emerging per quantum absorbed is of the order of 1 in 1000.

A simple explanation of all these facts is that, in those cathodes for which P and L are nearly equal, most of the energy is absorbed at a distance from the surface so great that the electrons have to undergo many collisions in reaching it. They lose energy in this process and most of them do not arrive with energy greater than the work function; and those that do arrive with energy greater than the work function have lost completely the direction of their original momentum. The efficiency of emission is therefore small, in spite of a large $D(W)$, and there is practically no variation of the emission with the direction of the electric vector.

There is one class of cathode which, although its emission is normal, has a large P/L ratio. This class consists of the thin films of the alkali metal upon less electro-positive supports that have been studied so carefully by Ives†. The films are so thin that they hardly change the optical properties of the underlying metal (e.g. platinum), and yet the photo-electric properties are largely determined by that metal. On our theory we must suppose that the function of the alkali metal film is simply to decrease the work function for electrons which have absorbed energy in the platinum and to increase greatly the transmission coefficient for all values of W in the neighbourhood of the work function. If the depth at which the electrons absorb energy in platinum were as great as that at which they absorb energy in potassium, we should still not expect the increase in $D(W)$ to be attended by any marked increase in P/L. But there are reasons for believing that the depth may be considerably less in platinum than in the alkali metals, and that a much larger proportion of the electrons that take energy from the light reach the surface without collision. If this is so, we should expect P/L to be much greater than for potassium and to vary in the opposite sense to the work function. This is what we find; as the thickness of the film increases the work function decreases, and P/L increases up to a maximum; after that maximum the work function increases and P/L decreases.

It appears therefore that a fair account can be given of the chief phenomena of normal emission by applying the conception of a transmission coefficient derived from the study of thermionics.

§ 3. SELECTIVE EMISSION

We turn now to selective emission. According to the fundamental conceptions of the theory, a maximum in the curve relating emission (reckoned on the basis of absorbed energy) to frequency of the radiation must mean selectivity either in the transmission coefficient or in the proportion of the absorbing electrons that approach the surface; those which take up a certain quantum energy must have a better chance of passing through the surface, or a better chance of approaching it than those which take up either less or more. The close association of selective emission with a high P/L ratio suggests strongly that the selectivity must be in the emission coefficients.

* L. Nordheim, *Z. f. Phys.* **46**, 11–12, 833 (1928).

† H. E. Ives, *Astrophys. Journ.* **60**, 209 (1924).

However, the work of Ramsauer and his followers shows that there may be selectivity in the passage of an electron among a mass of atoms; the second alternative is not therefore wholly excluded a priori. An examination of the condition in which selectivity appears makes it highly improbable, for the work of Pohl and Pringsheim* and of Fleischer and Dember† proves that the selective emission of potassium (and of all alkali metals) is due to a state of its surface, probably the presence of a gas film. This film affects somewhat the optical properties of the underlying metal, but not enough to change its general nature. There seems no reason to suppose that the layers that the electrons have to traverse before they reach the surface are not substantially the same whether there is or is not selective emission. We must conclude therefore that the selectivity arises in their passage through the surface.

Accordingly the problem of selective emission, the crux of any theory of the photo-electric effect, must be approached from two sides. We must determine what is the constitution of a surface that gives rise to selective emission, and we must inquire whether the theory of the transmission coefficient can explain why such surfaces transmit selectively. The first part of the problem alone will be considered here.

There are three classes of selectively emitting cathodes, which have been studied sufficiently for some idea of their constitution to be obtained:

(*a*) alkali metals with a gas film, probably oxygen, as just mentioned,

(*b*) alkali metals sensitised by the Elster-Geitel process of the discharge in hydrogen; or by Ives' method‡ involving the use of sulphur,

(*c*) thin films of the alkali metals on oxidised supports of other metals, as studied by Campbell§ and Koller‖.

It may be noted that cathodes (*b*) and (*c*) are unavoidably optically matt, and that it therefore cannot be definitely ascertained whether their P/L ratio is high; but it is permissible to assume by analogy that it is. Each class is characterised by the presence of an electronegative element; for hydrogen, since it forms salts with the alkali metals, may here be counted electronegative. On the other hand, surfaces known to be free from such elements do not show selective emission, even if the outermost layer is a thin film (Ives). Accordingly, we conclude that selectivity is connected with the presence of an electronegative element.

The part played by this electronegative element is suggested by recent work on thermionic emission. Kingdon and Becker¶ have shown that a thin layer of oxygen may act as a cement binding a monomolecular layer of a more electropositive element B (e.g. caesium) to a less electropositive element A (e.g. tungsten), and that the work function of the surface so composed is not only less than that of A but also less than that of B when in the massive state. Ryde**, in his very complete study of

* R. Pohl and P. Pringsheim, *Verh. d. deutsch. Phys. Ges.* **16**, 336 (1914).

† R. Fleischer and H. Dember, *Z. f. techn. Phys.* **7**, 133 (1926).

‡ H. E. Ives and A. L. Johnread, *Journ. Opt. Soc. Amer.* **20**, 11 (1930).

§ N. R. Campbell, *Phil. Mag.* **6**, 633 (1928).

‖ L. R. Koller, *Gen. Elect. Rev.* **31**, 476 (1928); *Phys. Rev.* **33**, 1082 (1929).

¶ K. H. Kingdon, *Phys. Rev.* **24**, 510 (1924); J. A. Becker, *Phys. Rev.* **28**, 341 (1926).

** J. W. Ryde—not yet published.

films of barium on oxidised and unoxidised tungsten, has extended this conclusion. He finds that the work function is less when B is bound to A by the cement of oxygen (or other electronegative element) than when B is deposited directly on A. Further, if a second monomolecular layer of B is deposited on the first, the work function is increased, until the work function characteristic of massive B is finally reached. Again, the attachment of a layer of B to its support is often stronger, the lower the work function of the composite surface; thus the first monomolecular layer of B adheres more strongly than the second and evaporates more slowly; and B adheres more strongly to its support when a layer of oxygen intervenes than when deposited directly on B.

With these facts to guide us our way is surely clear. In all the classes showing selective emission, with the possible exception of the alkali metals sensitised by hydrogen, the work function of the surface, as measured by the threshold, is less than that characteristic of the alkali metal concerned in the production of the cathode, when this metal is in the massive state. We must conclude that the electronegative element acts as a cement intervening between a film (probably monomolecular) of the alkali metal on the outside and a massive supporting metal on the inside; in classes (*a*) and (*b*) this supporting metal is the same as that forming the surface film, in class (*c*) it is probably different.

According to this view, Elster and Geitel's original theory of sensitisation (which they quickly abandoned and spent vain efforts subsequently in trying to destroy) was not so far wrong. The union of potassium and hydrogen, which leads to the formation of a definite compound, potassium hydride, in the massive state, does play an important part in the process. But the film of united potassium and hydrogen is probably so thin that the conception of a chemical compound is inapplicable; moreover, this film does not lie on the outside; it intervenes between the massive metal in the interior and a layer one molecule, or possibly a few molecules, thick on the outside.

Though this construction of the photo-electric surface is strongly indicated, definite experimental proof is lacking. The experiments are much more difficult than in the thermionic case, especially when the underlying metal is of the same nature as that which forms the film, but such knowledge as is available is at least consistent with the view suggested. The cathode which is easiest to study and probably has been studied most is Koller's caesium on silver oxide. It may be well therefore to describe the formation of such cathodes in detail; for it seems that most features of the process are general and are to be found in the formation of other alkali metal films on oxidised supports, e.g. potassium on copper oxide.

§4. THE CAESIUM-ON-SILVER CATHODE

In the preparation of such cathodes, the silver surface is first oxidised, caesium is next introduced into the cell, and finally the cell is baked, while still on the pump, to a temperature of about 200° C. The exact temperature is not important; the speed of the changes increases with the temperature, but a limit to the permissible temperature is set by the decomposition of the silver oxide before the changes have time to occur.

The changes depend upon the amount of caesium introduced. In order to describe them it will be convenient to suppose that the second and third stages are combined, and that the caesium is introduced gradually when the cell is being baked, but in such a way that it cannot escape into the pump before it has time to produce its effect.

We start then with the oxidised silver surface. The oxidation has to be carried so far that a layer of oxide at least 10 molecules thick is formed on the surface and displays interference colours similar to those of oxidised steel; the best colour to start with is a shade of blue, but thicker layers may be employed. The first effect of the caesium is to change this colour to a dark brown, which gradually spreads over the surface as the quantity of caesium is increased. At the same time the cathode acquires a photo-electric emission to visible light and a thermionic emission appreciable at 200° C. The photo-electric and thermionic currents increase with the area of the cathode that has changed colour, but less rapidly; that is to say, when half the surface has changed colour, the currents will be much less than half the values they attain when the colour change is complete. When it is complete, the cathode has the photo-electric emission characteristic of cathodes of this type, with marked selective emission in the neighbourhood of 700 mμ.

The quantity of caesium necessary to carry the cathode to this stage depends on the quantity of oxygen originally absorbed by the silver. It is not easy to determine accurately the requisite ratio of Cs to O; but it is certain that the amount of Cs required increases (within wide limits) with the amount of O absorbed, and that the ratio does not differ very greatly from that required to form the compound Cs_2O. The state of the cathode at this stage will be called state *A*.

The addition of more caesium produces a remarkable change. The dark brown surface changes very rapidly to a light grey, often with a pink tinge. At the same time the photo-electric emission to white light and the thermionic emission at 200° decrease greatly. Further there are signs that excess caesium is present; the metal may actually be visible in the cooler parts of the cell, or may show its presence by an insulation leak across the glass surfaces. If the supply of caesium is now stopped, while the baking is continued so as to drive out the excess caesium, the photo-electric and thermionic emissions rise once more and may eventually attain the values prevailing in state *A*. But there is a difference between the new state (state *B*) and the old. If the cell in state *A* is filled with helium or argon, and a discharge is passed through it, the photo-electric emission will be decreased somewhat, or at least will not increase. On the other hand, when state *B* has been reached, the discharge will generally increase the emission and raise it to a value definitely greater than that characteristic of state *A*.

If the supply of caesium is continued after state *B* is reached, the colour of the plate will become still lighter and will eventually attain an appearance indistinguishable from unoxidised silver. Stoppage of the supply of caesium and the removal of excess by baking will not now restore the photo-electric and thermionic emission; the cathode has now more nearly the properties of a film of caesium on pure silver; in particular the selective emission will be greatly diminished and the peak will move towards the shorter wave-lengths.

Such are the facts; now let us try to interpret them. In the first stage the caesium reacts with the silver oxide to form Cs_2O (which is brown) and reduced silver. But Cs_2O is not the photo-electrically active substance; for the activity is not proportional to the area formed; moreover the admission of pure oxygen, which would not react with Cs_2O, destroys the activity. The activity arises more probably from a layer of caesium on the surface of the Cs_2O-Ag mixture; it does not develop as quickly as the change of colour, because there is no excess of caesium to form a layer until the reduction of the silver oxide is nearly complete. The only effect that is likely to ensue from the passage of an electric discharge and the bombardment of the surface with positive ions is the removal of part of the caesium film; the activity therefore decreases, or at least does not increase.

The changes involved in the passage from state *A* to state *B* are much more puzzling. Of course it is possible to postulate the formation of a sub-oxide (a sub-oxide of potassium has been described); but there is no evidence that the passage from the end of state *A* to state *B* requires the supply of any additional caesium. Indeed there is some evidence (though it is not complete) that the sudden change in the appearance of the surface is accompanied by the liberation of some of the caesium that had been absorbed previously and by its reappearance in the metallic state; moreover, the final state of the surface, when the supply of caesium is continued, is almost certainly pure silver, except, of course, for films too thin to affect the optical properties. An equally plausible explanation is that there is some re-arrangement of the atoms in the Cs_2O-Ag complex which results in the oxygen atoms being set free from their chemical combination with the caesium, and allows them to form a surface film on some underlying combination of silver and (possibly) caesium. The excess caesium is then free to form a layer on the oxygen. The excess is so great that a layer several molecules thick is formed, and the photo-electric properties approach those of massive caesium, which is relatively insensitive. Further baking removes much of this excess, and reduces the thickness of the layer; if it is sufficiently prolonged it may leave only a single layer, which is particularly firmly attached. If the reduction to a single layer is not complete, it is effected by the bombardment of positive ions in the discharge. The discharge develops the highest activity because it reduces the surface to a single layer of caesium atoms resting on the oxygen layer.

Here it may be interesting to observe that, though none of the other stages here discussed can be traced in selective emitters of classes (*a*) and (*b*), this last stage can sometimes be traced. It is known that the emission of the potassium surface sensitised in hydrogen is increased temporarily by a discharge in argon or helium, such as occurs when a gas-filled cell is raised above its sparking potential. This increase again we may suppose to be due to the removal of layers of potassium in excess of the single layer that gives the maximum emission. There is no considerable change of the threshold in this case; but the threshold of the sensitised surface is not markedly different from that of the unsensitised. We must suppose that the layer of hydrogen, unlike the layer of oxygen, though it increases the transmission coefficient, does not greatly affect the work function.

§ 5. CONDITIONS FOR SELECTIVE TRANSMISSION

It seems then that there is nothing to prevent us from at least supposing that the surfaces that give selective emission are compounded of layers in the manner suggested by the thermionic analogy, and that the function of the electronegative element is to intervene between the supporting metal and the monatomic layer of highly electropositive metal. The second question now arises, and we have to ask why a surface constituted in this manner should transmit selectively. Here a hint may be drawn from a recent remarkable result of Fowler and Wilson*. In discussing the passage of alpha particles through atomic nuclei, they conclude that particles of one particular velocity ought to pass practically without hindrance. They are those

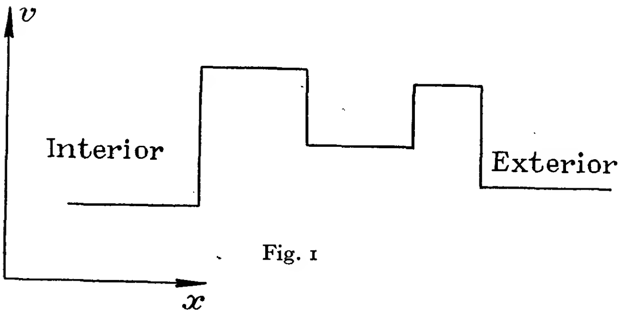


Fig. 1

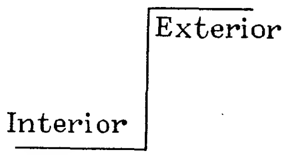


Fig. 2

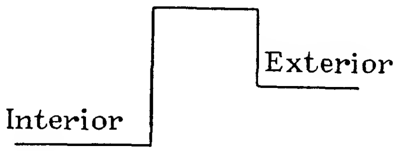


Fig. 3

particles that are associated with waves of a length such that they can form standing waves between the two potential discontinuities of the same sign that may be taken as representing the boundaries of the nucleus. Generalising this result†, we may say that a surface will transmit selectively if the potential changes at its surface are distributed in the manner shown in Fig. 1, and if there is in that diagram a valley between two peaks; the standing waves form between the sides of the valley. In the diagram distance x along the line perpendicular to the surface is measured horizontally, and the potential v at any point vertically.

Now is it reasonable to suppose that such a diagram represents the conditions in such a series of layers as we have supposed? The diagram corresponding to a clean metal surface is that of Fig. 2, and that corresponding to a surface with monatomic oxygen film (such as monatomic layer of oxygen on tungsten) is probably

* R. H. Fowler and A. H. Wilson, *Proc. R. S.* **124**, 493 (1929).

† At this stage in the argument I had the advantage of consultation with Mr R. H. Fowler, and the remaining ideas are his rather than mine. He is developing the subject mathematically in a publication in the *Proceedings of the Royal Society*, which will appear at about the same time as this paper.

that of Fig. 3; Fig. 3 certainly represents a layer of an electropositive metal (such as barium) on a monatomic oxygen layer that rests again on a less electropositive metal. If we take two diagrams similar to Fig. 3, and, reversing one of them, join them together, we get Fig. 1. It seems possible therefore that we might obtain the desired form of our diagram, if we supposed that the selectivity emitting layer has one of the following constitutions:

$$A\text{—}O\text{—}O\text{—}B \quad \text{or} \quad A\text{—}O\text{—}B\text{—}O\text{—}B;$$

here A is the less electronegative metal, each O a monatomic layer of the electronegative element, and B a monatomic layer of the more electropositive metal. Such a constitution, and more particularly that which has a B in the middle, seems entirely in accordance with our analysis of the facts. If that analysis is correct, the problem of selective emission appears soluble, if only detailed calculation will show that the order of the magnitudes concerned is correct. For the investigation of that question, Fowler's paper already mentioned should be consulted.

THE STANDARDISATION OF PHOTO-ELECTRIC CELLS

By N. R. CAMPBELL.

(Communication from the Staff of the Research Laboratories of the General Electric Company Limited, Wembley.)

MS. received April 11, 1930. *Read June* 5, 1930.

ABSTRACT. The photo-electric cells offered for sale by different makers are so different and so differently described that some standardisation is urgently necessary. The type of gas-filled cell that is now widely used for the reproduction of talking films and similar purposes ought to be standardised in respect of size, arrangement of terminals, and running voltage. Other types of cells should not be standardised at present in this sense. But standard methods of describing the performance of all cells are desirable. Proposals are made for standard descriptions of the emission and of the characteristic of gas-filled cells.

§ 1. TWO KINDS OF STANDARDISATION

PHOTO-ELECTRIC cells are now regular articles of commerce, but there is very wide divergence in their manufacture. There are some purposes for which every maker of photo-electric cells offers to provide cells; and yet those made by different makers for the same purpose agree in hardly a single feature. The object of these notes is to suggest that it is desirable that photo-electric cells should be standardised in some respects at least.

Standardisation may have two objects. It may seek to fix by convention certain properties of the standardised article, or it may seek to establish some agreed system of describing its properties. The two kinds of standardisation are, of course, properly applicable to different kinds of properties. The first kind is applicable to properties that do not affect materially the efficiency of the article or to those that affect it so little that the gain arising from uniformity is greater than the loss arising from standardising any but the most efficient form. The second kind is applicable to the properties that directly determine efficiency.

In the matter of photo-electric cells there is room for both these kinds of uniformity. A very large proportion of the cells sold at the present time (perhaps 90 per cent.) are used for the reproduction of talking films and for picture telegraphy. The efficiency of cells for these purposes is not affected very greatly by their geometrical form or by the arrangement of their terminals, while any lack of uniformity in this matter makes it impossible to substitute the cells of one maker for those of another; users of cells and, in the long run, all but the least competent makers must suffer from this lack of interchangeability. Here is a clear case for the first kind of standardisation. On the other hand, the standardisation in this sense

of the cathode emission, which is one of the main factors determining the efficiency of the cell, would be disastrous to progress. Here, however, there is room for a standardisation of the second kind which would persuade makers to give data of the emission that they offer according to some uniform system, so that the promise of one maker may be directly compared with that of another.

§ 2. STANDARD GAS-FILLED CELLS

Let us start with the first problem and consider, first, size and shape.

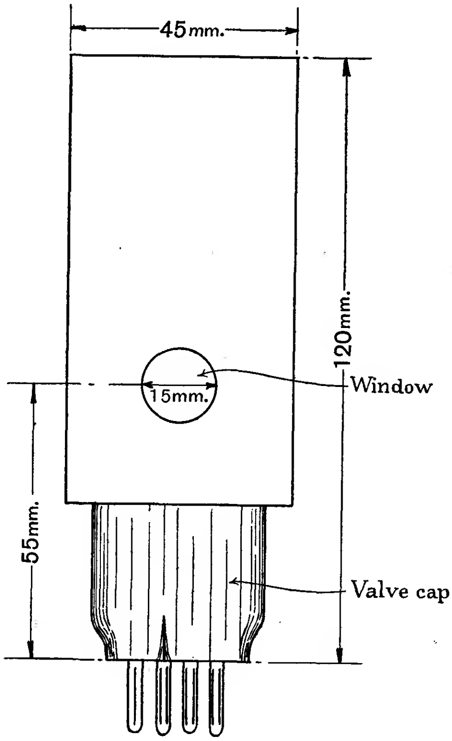
Designers of talking-film and picture-telegraphy apparatus like their cells to be small. On the other hand, there is a limit to the size of cells below which they become difficult to make and—possibly this is not exactly the same limit—below which the highest efficiency is unattainable. Maximum dimensions for cells and minimum dimensions for the apparatus to take them should therefore be fixed, preferably in the form of the dimensions of a cylinder enveloping the cell. For the diameter of this cylinder 45 mm. may be suggested. Some existing cells have greater diameters and some existing apparatus smaller diameters; but this appears to be a reasonable compromise between the needs of makers and users.

The length of the cylinder will be determined in part by the terminals and by the optical arrangements. The use of a standard 4-pin valve cap for at least one of the terminals is becoming general; it should be prescribed universally, for it provides the most convenient way of supporting the cell in a fixed position. It is less certain whether both terminals should be connected to separate pins on the same cap. The objection to this plan is insufficient insulation. There is no difficulty in obtaining an insulation resistance of 10 megohms, which is sufficient when the cell is to be used with rapidly varying lights; for then it is necessary to connect across the cell a resistance of not more than 1 megohm. But cells of this type, though primarily intended for use with such lights, are also suitable for other purposes, which may require an insulation resistance of at least 100 megohms; this is not easily attainable when both leading-in wires are brought out at the same end of the cell into the same cap. However, it may be observed that the leads, even if they are not brought out at the same end of the cell, may be connected to pins on the same cap by means of an exterior wire; this wire can be severed and separate connexion made, if higher insulation is required. Accordingly the question may be left to the decision of users. If a second terminal, independent of the valve cap, is used, it should be a screw terminal of standard size, and a convention laid down as to which of the terminals is to be the anode and which the cathode.

The position of the window must now be fixed; by "window" is here meant generally the part of the wall of the cell on which the light should fall so as to strike the cathode in the most appropriate fashion. The centre of the window should be at some standard distance from the bottom of the valve cap and the top of the base into which the pins of the cap fit. 55 mm. may be suggested here; this would bring the centre about 25 mm. above the junction of the valve cap and the glass of the cell; but valve caps differ a little in length. Further the area of the window should be prescribed. So long as all the light enters the window, the efficiency of the cell

generally increases somewhat as the area of the window is diminished; hence a minimum area should be prescribed. It is probably sufficient that the cell should use efficiently all the light falling on a circle 15 mm. in diameter.

When these matters are fixed, makers will not differ very widely in the overall length of the cell, although those who prefer the cylindrical form will want more length than those who prefer the spherical. The length of the enveloping cylinder might be fixed at 120 mm. The framework into which the maker will have to fit his cell and for which the user will have to provide in his apparatus will then be that shown in the accompanying figure.



Lastly, there is the anode voltage. Here, at present, there is wide divergence of practice. Some cells on the market cannot be used with voltages as high as 100, others are apparently designed for voltages greater than 300. A low anode voltage presents advantages to the user who has to provide the H.T. supply, but, if it is very low, it necessarily involves some sacrifice of efficiency. Up to a certain limit, increase of anode voltage, and consequent decrease of the pressure of the gas-filling, can be made to give greater magnification, especially under light varying with high frequency. Accordingly it is desirable to fix the standard voltage as high as other considerations permit.

In the circumstances in which cells of the type that we are considering will be used, it is probably necessary to suppose that the cell will be connected permanently to the standard voltage. The cells are liable to be subjected occasionally to very

great illuminations, and it is necessary that they should be made so that a glow discharge cannot be maintained in them by this voltage, however great the illumination; that is to say, the standard voltage must be less, not only than the starting voltage of the discharge, but also than its stopping voltage. Since the illumination to which the cells are subjected in normal use is so small that, if they were to be subjected to no greater illumination, they could be used at voltages approaching very nearly the starting potential in the dark, the limitation thus imposed involves a very considerable sacrifice of output; the current will often not be as much as a quarter of what it might be if the voltage could be adjusted to the illumination. This is probably unavoidable; but makers of cells should aim at making the difference between the starting and stopping potentials as small as possible, and the magnification below the stopping potential as great as possible, so that the sacrifice may be as small as possible. Of course the limitation of the voltage applied to the cells in this particular connexion will not prevent users who can work with adjustable voltages using them at full efficiency.

§ 3. OTHER CELLS

Cells made according to this standard specification would serve for many purposes other than that for which they are primarily intended. But they would not serve all purposes. In the class of gas-filled cells intended for use with white light, very much larger cells are occasionally required (e.g. for television by the scanning-spot method) and also very much smaller cells. Further, there are the distinct classes of vacuum cells intended for accurate measurement and of cells for use with ultra-violet light. But the number of these cells sold is so small and the variety of the purposes to which they are put is so large that it would be unwise to attempt at present any standardisation of the first kind.

§ 4. SPECIFICATION OF EMISSION

We turn now to standardisation of the second kind, that is to say, the prescription of standard methods of stating the properties of cells.

The most important property is the relation of the current through the cell to the illumination. This relation depends, of course, on the nature of the light and on the voltage applied to the cell. In vacuum cells the second factor needs no consideration; the voltage for which data are given should be the saturation voltage. Further, since in vacuum cells the current is closely proportional to the illumination, when the nature of the light is constant, the relation should be described by giving the emission, that is to say, the ratio of the saturated current to the rate at which radiation falls on the window. Since this ratio varies somewhat with the mode of incidence of the illumination, perpendicular incidence upon the window of the cell should be specified. There still remains some ambiguity, because the cathode is not always uniform over its surface, and the emission may vary with the part of the window illuminated; the average value should be given, obtained by an illumination uniform over the whole window.

For scientific purposes the most suitable way in which to describe the variation of the emission with the nature of the light is to give a curve relating σ_λ and λ, where σ_λ is the emission for wave-length λ. But the question of units remains. σ_λ is sometimes given in coulombs per calorie, sometimes in coulombs per erg, and sometimes in amperes per watt. The first method has historical priority, but it is less convenient practically than the third, which is, moreover, the method universally adopted for stating thermionic emission.

When cells are to be used with visible light, this is not the best method for practical purposes. The light to which such cells are most often subjected is that from a gas-filled incandescent lamp, and data referred to this light are essential. The colour temperature of the tungsten filament may vary from 2600° K. to 3100° K., according to the size and life of the lamp; it would probably be sufficient to take as a standard a single temperature, say 2800° K. The emission for such light should be given in amperes per incident lumen, or per incident watt; lumens are to be preferred, partly because lamps are now usually rated in lumens, partly because, if watts are used, there is liable to be confusion between the watts consumed in the lamp and the watts radiated by it. Further, if a spectral distribution curve is given (and it is desirable), it should take into account the distribution of energy in the spectrum of this source. A curve giving simply σ_λ is misleading, because it fails to take into account the much smaller amount of energy available at the shorter wave-lengths. If such a curve is given for a potassium cell and a caesium-on-silver oxide cell, the maximum of the potassium curve is higher than that of the caesium, and it might be concluded that their emissions under white light were of the same order; actually that of the caesium is much higher, because its maximum lies in a region where far more energy is available. We suggest that the ordinates of the curve should be, not σ_λ, but $\sigma_\lambda P_\lambda$, where P_λ is proportional to Planck's function for the standard temperature. The area under the curve between two ordinates will then be proportional to the current obtained in response to that part of the radiation from the source which would be isolated by a filter perfectly transparent between these ordinates and opaque elsewhere. The factor of proportionality should be stated by giving the factor by which the product of this area in cm.^{2} by the incident illumination in lumens (or alternatively in watts) must be multiplied, in order to obtain the current in amperes (or alternatively microamperes). On the other hand, when the emission outside the visible spectrum, and particularly in the ultra-violet, is given, there is no reason to give anything but σ_λ; for the illuminants used vary so greatly in their spectral distribution that this will always have to be taken into account in estimating the current.

Less complete methods of stating the spectral distribution of the sensitivity are also worthy of consideration. Thus there might be given the mean emission for each of a series of wave-length ranges, e.g. 700–600, 600–500, ... mμ; or the range of wave-length over which the emission does not fall below some prescribed minimum, together with the wave-length for maximum emission; or any of the other alternatives that will suggest themselves. If such methods are adopted, the emission should be given in amperes or microamperes per watt of energy incident on the window.

§ 5. SPECIFICATION OF CHARACTERISTIC

In gas-filled cells, on the other hand, the effect of voltage must be taken into account. For the standard gas-filled cells considered earlier, the current for some standard illumination (e.g. 0·1 lumen) at the standard voltage will suffice, but others will require more information. This information is often given by a series of characteristic curves of the cell (i.e. curves relating current and voltage) for a series of different illuminations. These curves are very useful and should be encouraged. The illuminations for which they are drawn should be standardised. When white light is to be used, the illumination should be given in lumens from the standard illuminants; curves for 0·001, 0·01, 0·1, 1·0 lumen are suitable. For cells to be used in the ultra-violet the illuminations are probably most conveniently stated in terms of the primary photo-electric current that they excite, so that the ratio of the ordinate to the figure marked on the curve gives the magnification due to gas-filling at the corresponding voltage. This method, however, is not wholly satisfactory. It gives the user more information than he wants—for a cell is seldom used at intermediate voltages—and it makes it difficult to take account of the inevitable variations between individual cells; it would be impossible to give a complete set of curves for every cell. It might be desirable therefore to supplement a set of curves generally representative of cells of a given type by some smaller amount of information relating to each cell. Thus there might be given the ratio of current to illumination

(1) at a voltage so low that it represents roughly the emission of the cathode,
(2) at the highest practicable voltage.

For (1) a voltage of 20 would be suitable; for though the current at this voltage is not always equal to the saturation current in the absence of gas, the ratio of this current to the saturation current does not seem to vary very greatly in cells of different types. For (2) it is necessary to define the highest practicable voltage. It might be taken as that at which the current increases by x per cent. (where x should be less than 10) for an increase of 1 volt in anode voltage, the illumination being so small that any further decrease of it does not change this figure. It is clearly desirable to choose a small illumination for this purpose, because it is then that the maximum voltage is most important.

Other properties affecting materially the performance of the cell are the insulation resistance, the "dark current," and the stability. In any specification on which the acceptance of cells is to be based some account should be taken of these. The first two are, of course, to be specified in ohms and amperes respectively; the third, which is (or ought to be) important only in gas-filled cells, should be determined by the change in current over some period (say 1 hour) when the cell is subjected to a prescribed voltage and illumination; it is also necessary to determine whether the cell is or is not to be raised to its glow potential before the stability is determined, for the stability is usually greater if the glow discharge is first passed.

THE MANUFACTURE, PROPERTIES, AND USE OF SODIUM PHOTO-ELECTRIC CELLS

By Dr P. SELÉNYI.

(Communication from the Tungsram Research Laboratory, Ujpest, near Budapest.)

MS. received April 23, 1930. *Read June* 4, 1930.

ABSTRACT. This paper contains the results of the photo-electric investigations carried out in recent years by the staff of the Tungsram research laboratories. After a brief description of the manufacture of ordinary sodium-cathode photo-electric cells by glass-electrolysis (C. R. Burt, L. Márton and E. Rostás) the author describes his own experiments on these cells, especially the two different methods found by him for making sodium cathodes red-sensitive. The first method, in which the sodium surface is covered with a very thin layer of nickel, results in high sensitivity lasting for a few hours only. The cells made by the second method, i.e. by introducing oxygen into the bulb by the electrolysis of the glass wall, keep the same valuable properties (red-sensitivity and high overall sensitivity) and last a very long time. The following sections of the paper are devoted to a discussion of the use of photo-electric cells for different purposes. The employment of alternating voltage for the measurement of photo-electric currents is dealt with, a few new methods for controlling electromagnetic relays by means of photo-electric cells are described, and the use of photo-electric cells for photometric measurements is discussed.

§ 1. INTRODUCTION

IT is now more than four years since, in the course of experiments carried out in our laboratory with regard to the electrolytic introduction of sodium into closed glass vessels*, it occurred to Dr L. Márton and Mr E. Rostás whether it would not be possible to make use of this most elegant method for the manufacture of photo-electric cells comprising a sodium cathode. Without having had any knowledge of the researches carried out by Mr R. C. Burt† with similar ends in view, they have worked out methods for the manufacture of such sodium photo-electric cells, their original intention having been to utilise these methods merely for the purposes of our own laboratory. Owing to our intimate relations with a number of manufacturing firms and scientific institutes, our photo-electric cells have gradually become well known, and demands for such cells have poured in from many different quarters. Under these circumstances our Works' Management has felt induced to organise the regular manufacture of these cells. This work has been entrusted to the author of this article, the two investigators named having in the meantime left our laboratory in order to take up new duties in laboratories, connected with our own by friendly relations, in other countries. Not only have the initial difficulties been overcome very quickly, but also we have been successful

* See, for instance, W. W. Loebe and W. Ledig, *Z. f. techn. Phys.* **6**, 287 (1925); also M. Pirani and E. Lax, *ibid.* **3**, 232 (1922).

† R. C. Burt, *Phil. Mag.* (6), **49**, 1168 (1925).

in improving considerably the quality of the cells, so that now our cells possess a number of properties which have proved extremely useful for various purposes. The methods of manufacture and the properties of these cells have been discussed in an article* by Márton and Rostás and in a short report† by the author of this article read at the Congress of German Physicists held at Prague in September 1929. The present article contains a short summary of the contents of these papers and, in addition, particulars of the results of our more recent researches of a more quantitative nature‡.

§2. MANUFACTURE AND PROPERTIES OF STANDARD SODIUM PHOTO-ELECTRIC CELLS

Our standard sodium cell, the product of gradual development on the basis of the researches carried out by the two investigators named, possesses the form and internal design shown in Figs. 1 and 2. The cell consists of a bulb 1 (Fig. 2) of spherical shape, made of glass free from lead, and an incandescent lamp stem, like-

Fig. 1. "Tungsram Nava" photo-electric cell.

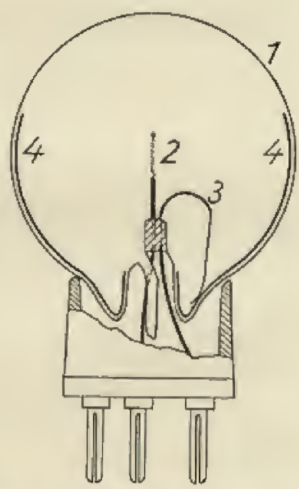


Fig. 2. Internal design of "Tungsram Nava" photo-electric cell.

wise made of glass free from lead, carrying three electrodes and sealed to the bulb. Two electrodes carry the filament 2; the third electrode 3 possesses an extension consisting of a piece of platinum-coated wire or Dumet wire, which is bent sideways towards the wall of the glass bulb. When the stem is sealed to the bulb, this extension piece adheres firmly to the wall of the glass bulb and acts as a leading-in conductor for the cathode 4 which is formed by condensation at the point in question.

* L. Márton and E. Rostás, *Z. f. techn. Phys.* **10**, 52 (1929).

† P. Selényi, *Phys. Z.* **30**, 933 (1929).

‡ The cells have already been placed on the market under the name of "Tungsram Nava" photo-electric cells." For the characteristics of the different types see Table 4 (at end of paper).

After the cell has been evacuated and fitted with a socket (the so-called standard "Europe" sockets for amplifier tubes are used), electrolytic introduction of sodium is effected. The arrangement used by ourselves was similar to that employed by various authors for this purpose; it is shown in Fig. 3 and is self-explanatory. The glass bulb is immersed in a molten mixture of salts (approximately equal proportions of $Na\,NO_3$ and $Na\,NO_2$) at a temperature of about 300° C. The filament is heated by means of low-tension alternating current and itself supplies the current, necessary for electrolysis, in the form of thermions. The current itself is maintained by means of a storage battery of about 300 volts, the positive terminal of which is

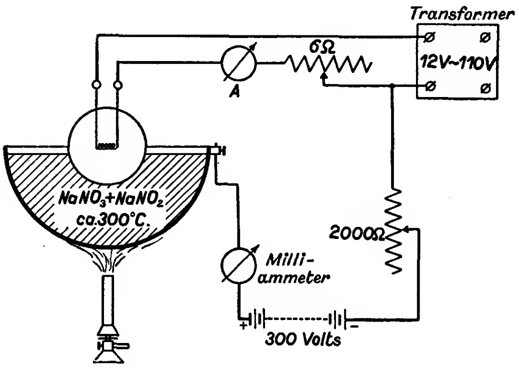


Fig. 3. Arrangement for electrolytic introduction of sodium into glass bulb of cell.

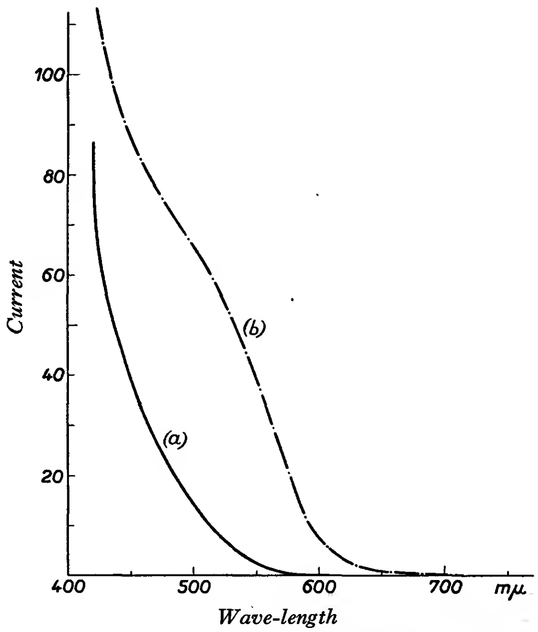


Fig. 4. Curves of spectral sensitiveness: (*a*) pure sodium cathode; (*b*) oxidised sodium cathode after very long use.

connected to the molten mixture of salts, whilst its negative terminal is connected to the filament. The intensity of the electrolysing current amounts to between 50 and 100 milliamperes. The whole cycle of operations necessary for converting the "lamp" into a "photo-electric cell" takes about 5 minutes only, during which time such parts of the bulb as are intended to serve for the condensation of sodium on them are cooled by a strong current of air. After a vigorous initial clean-up the electrolysis takes place very rapidly. The properties of these cells correspond to the well-known photo-electric behaviour of sodium. The spectral sensitivity has the form shown in Fig. 4, curve (a); the long-wave limit is situated at about 570 mμ and the total sensitiveness for the white light of an incandescent lamp of filament temperature about 2700° *K*. amounts to from 2 to 4×10^{-10} A. per lux, or 0·1 to $0{\cdot}2 \times 10^{-6}$ A. per Hefner lumen.

§ 3. CONDITION OF SURFACE AND SENSITIVENESS

The sodium cathodes produced in the manner described are of a silvery white colour; they present a bright mirror-like surface on the glass side and a finely granulated dull surface on the inner side. The correct surface condition of the sodium deposit is decisive for the amount of sensitiveness; the more mirror-like the surface, the smaller the total sensitiveness, whilst its spectral distribution remains the same. The correctness of this assertion can be proved most conclusively by carefully increasing the temperature of the cell until the sodium deposit begins to melt; the surface of the latter becomes mirror-like by this process, and the sensitiveness is reduced to practically zero.

The surface condition of the sodium deposit—whether mirror-like or of a finely granulated dull description—depends not only on the degree of vacuum and on some other circumstances difficult to define, but also in a decisive manner on the

Fig. 5. Shadow phenomenon on sodium cathode.

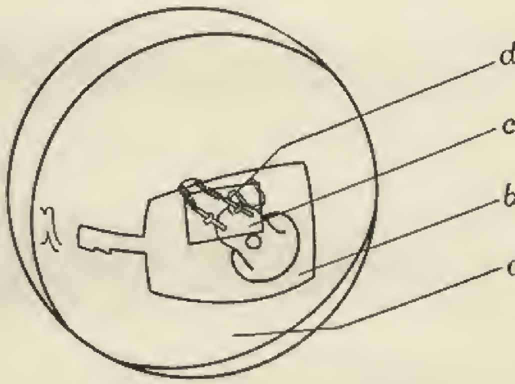


Fig. 6. Contour drawing of Fig. 5.

temperature and on the surface condition of the glass wall on which the deposit condenses. This is already partly evident from the paper by Messrs. Márton and Rostás to which reference has been made. These investigators observed the remarkable phenomenon* that if the glass is powerfully cooled the sodium will generally condense so as to present a dull surface, whilst some portions of the sodium deposit will present a mirror-like surface. The areas on which these two different types of condensation take place are separated by sharply defined boundary lines, as shown in Figs. 5 and 6, reproduced here from the paper quoted. The central part *b* (Fig. 6) of the sodium deposit is mirror-like, while the outer part *a* presents a uniform finely-granulated dull aspect; *c* is a small mica plate fitted below the filament. Careful observation reveals the fact that the mirror-like portion of the surface represents a central projection of the small mica plate and of the left-hand electrode, the point marked *d*, i.e. the point where the filament is welded to the right-hand electrode, figuring as the centre of projection. At the

* L. Márton and E. Rostás, *loc. cit.* p. 53.

time when it was first noticed, this phenomenon was observed in a very large number of cells and we surmised that it had some connexion with molecular rays issuing from the point d; attempts to explain the phenomenon remained, however, unsuccessful. Our recent experiments have confirmed our surmise and have shown that the shadow phenomenon appears only when the filament is subjected to an overload of such magnitude as to cause the welding spots on one or both ends of the electrodes, which consist of nickel, to become incandescent. In a good vacuum, the nickel evaporating from these spots sets up molecular rays by the action of which a shadow of the inner parts of the cells is produced on the bulb wall. The shadow cast by the molecular rays is subsequently "developed" and rendered visible by the sodium deposit in the usual well-known manner, the sodium condensing on the clean glass surfaces in a manner different from that in which it condenses on spots covered with a layer of nickel. We have found the correctness of this theory confirmed in a very large number of cells; amongst other instances it may be mentioned that the occurrence of duplicate shadows, observed already by Messrs Márton and Rostás in some cases, fits in very well with this theory.

§ 4. OBSERVATIONS ON SODIUM CATHODES COATED WITH A THIN LAYER OF NICKEL

The observations to be described in this section bear, as I have subsequently found, a close relation to the researches of a similar nature carried out by Dr H. E. Ives* on the photo-electric properties of thin layers of alkali metals. To quote only what is of immediate interest for us, Ives has found that "the long-wave limit of the emission first moves toward red as the film increases in thickness and then after the maximum of photo-electric sensitiveness is passed, moves back toward the violet." This cycle of variations is performed within a period of about two or three days. Our own observations accord herewith qualitatively very well. The nature of our experiments and their results are, however, somewhat different from the quantitative point of view. The observations made by Ives refer to layers of sodium which are produced by spontaneous deposits formed on a metal plate (platinum foil) previously cleaned by heating it to incandescence, i.e. by a process of distillation. Our own experiments have, as against this, been made in such a manner that the cathode consisting of sodium has subsequently been coated with a very thin layer of another metal, particularly with a layer of nickel, and the variation of the photo-electric properties of the cathode with time has been observed. For all the experiments our standard sodium cells shown in Figs. 1 and 2 have been used; the coating with a layer of nickel has, as described above, been effected simply by subjecting the filament to an overload. The layers produced were quite thin, being recognisable on the bulb in the form of a very slight blackening only.

After such preparatory treatment a succession of phenomena, as described already by Ives, takes place in the cell: the total sensitiveness is increased, the long-wave limit is shifted toward red, reaches a certain "most favourable" condition, and returns again to its original position. It cannot be doubted that these modifications are caused in this case, as well as in the case of the experiments

* H. E. Ives, *Astrophys. Journ.* **40**, No. 4, 209 (1929).

made by Ives, by a gradual deposit of a layer of sodium being formed on the layer of nickel; the most favourable condition most probably corresponds to the existence of a layer of approximately mono-molecular thickness.

The way the process takes place as a function of time depends on various circumstances, in the first place on temperature. In many cases, especially if the cell has not been cooled to a sufficient extent during the preparatory treatment, the cell will be very "active" immediately after it has gone through this treatment, and in this case it is only the retrograding part of the process which may be observed. For this purpose the photo-electric current of the cell produced by a 100-watt gas-filled lamp, has been measured (in microamperes) from a distance of a few centimetres. The photo-electric current I_w generated by the total white light was first measured and then the photo-electric current I_r generated by the red light. The red light was obtained by inserting an ordinary ruby glass plate of a lighter description (transmitting above about 600 mμ). $R = 100 I_w/I_r$ can be called the "relative sensitiveness for red." Table 1 gives particulars of such a case (cell No. 7720).

Table 1. Variation of relative sensitiveness for red with time (Cell No. 7720).

Time hr.	Time min.	I_w	I_r	R per cent.
0	00	15	—	—
0	01	47	4·8	10·0
16	—	45	4·2	9·3
63	—	21	1·5	7·1
65	—	19	0·9	4·7
70	—	15	0·5	3·3
87	—	12·4	—	—
111	—	12·0	—	—

The cell had before treatment been giving a total photo-electric current $I_w = 15\,\mu$A, which immediately after treatment rose to three times its original value, namely to $I_w = 47\mu$A. At the same time a high degree of sensitiveness against red, amounting to 10 per cent., becomes noticeable; both values subsequently decrease gradually, viz. at a slower rate in the first 63 hours and rapidly afterwards. This was the consequence of a variation of temperatures employed on purpose. In particular, it has been found that the whole process depends very much on temperature; by increasing the temperature the process is considerably accelerated, whilst by diminishing the temperature the process is retarded. In the case described the cell was kept at a temperature of 0° C. during the first 63 hours. It will be seen that the "dis-activation" takes place at an appreciably slower rate than later on when the cell was brought up to room temperature. Still more striking is the retarding influence of temperatures which are lower still; at the temperature of solid carbonic acid it is possible to let the cell "freeze," so to speak, in which case the cell will remain during a considerable time in the condition it happens to be in, with hardly any change occurring. If subsequently the cell is again brought up to room temperature, it returns to its original condition within

a day or two; with cell No. 7740, for instance, the following results were obtained. Immediately after treatment, the cell gave $I_w = 35\mu A$, $I_r = 3{\cdot}2\mu A$, $R = 9{\cdot}1$ per cent. The cell was subsequently stored in solid carbonic acid and after four days gave $I_w = 36$, $I_r = 3{\cdot}5$, $R = 10{\cdot}0$ per cent.; after the lapse of a further four days it gave $I_w = 25$, $I_r = 2{\cdot}8$, $R = 11{\cdot}5$ per cent. The cell was now brought up to room

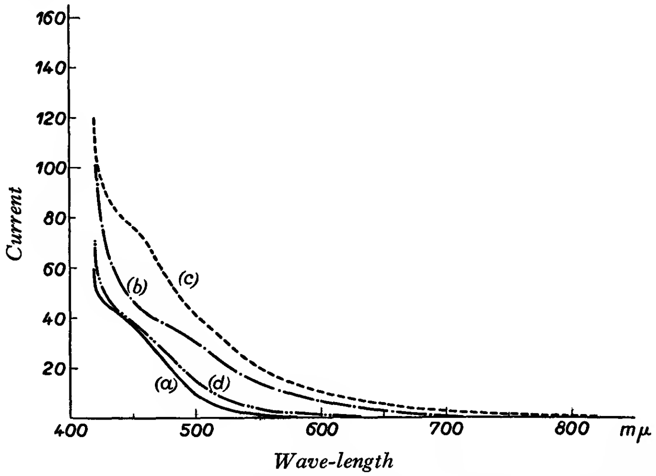


Fig. 7. Curves of spectral sensitiveness of sodium cathodes treated with nickel: (*a*) 20 minutes after treatment; (*b*) 80 minutes after treatment; (*c*) 130 minutes after treatment; (*d*) 22 hours after treatment.

Table 2. Variation of relative sensitiveness for red with time (cell No. 7740).

Time hr.	min.	I_w	I_r	R per cent.	Curve in Fig. 7
0	0	7	—	—	
0	30	9·2	—	—	(*a*)
0	45	13	0·2	1·5	
0	57	18·2	0·4	2·2	(*b*)
1	35	25	0·8	3·2	(*b*)
1	40	27	1·0	3·7	
2	04	30	1·5	5·0	(*c*)
2	29	35	2·0	5·7	(*c*)
2	35	30	1·8	6·0	
22	—	16	0·2	1·2	(*d*)
49	—	10	0·2	2·0	

temperature; in 3 days I_w diminished again to $14\mu A$ and the sensitiveness for red had disappeared. This effect of temperature can no doubt be attributed to the variation with temperature of the vapour tension of sodium.

It should be noted that it is possible to repeat this whole process several times. The figures contained in Table 2 were likewise observed with cell No. 7740 on the occasion of a previous test, when the curve of spectral distribution (see Fig. 7) was also recorded over its whole range.

The curves, as usual, refer to a spectrum possessing uniform distribution of energy; as the energy measured by means of a thermo-element was very small in

the violet part, these parts of the curve are not particularly exact. As may be seen, a secondary maximum, or whale-back of the curve, appears in the course of "activation" in the neighbourhood of 450 to 500 mμ, and the long-wave limit is displaced in the most favourable case as far as over 800 mμ. Both results have been confirmed by repeated experiments. The second result definitely contradicts what has been found by Messrs Ives and Olpin*, according to whom "the wave length of the maximum excursion of the photo-electric long-wave limit was found to coincide with the first line of the principal series, i.e. the resonance potential."

We are unable to state the reason of this discrepancy, particularly whether perhaps it may be attributed to the influence of any gas being given off by the nickel electrodes. In any case our results may be reproduced with any "Tungsram-Nava-N" cell as obtainable on the market.

We have so far repeatedly used the expressions "activation" and "dis-activation." Our reason for doing so is that the phenomena described bear a close affinity to similar phenomena of "activation" observed by Langmuir on thorium-coated tungsten filaments. It may be left undecided whether the covering-up of the nickel layer in our experiments is due to the diffusion of the sodium through the layer or to the evaporation of the sodium at the places which have remained free from nickel; at any rate the phenomena observed must be attributed in this case as well in the case of thorium-coating to a diminution or increase respectively of the work function of the electrons.

§ 5. OBSERVATIONS ON OXIDE-COATED SODIUM CATHODES

When comparing the results given above with the experience gained in connexion with the manufacture of glow cathodes covered with oxide, one is led to the conclusion that a layer of sodium covered by oxide would perhaps possess, in a still greater and permanent measure, the favourable properties referred to above. We have started from this idea and our experiments have indeed confirmed these expectations. These latter experiments carried out by us bear—as we subsequently found—the same relation to experiments of a similar nature carried out by N. R. Campbell†, as the nickel-sodium experiments to the researches effected by Ives. We have, however, been able to carry out our experiments, especially the oxidation of the alkali metal, under much more clearly defined conditions, and accordingly our results may be reproduced in full.

Some time ago I showed‡ that it is possible to introduce oxygen into a closed glass vessel by subjecting the glass wall to electrolysis, a gas contained in the vessel and ionised by an electric discharge being used as an anode. By modifying this method of procedure to some extent, we are now able to carry out this electrolysis of the glass in the case of an evacuated bulb also. When using this method in its suitably modified form, our tests were carried out in such a manner that, the cells having been evacuated and sealed off, sodium was first introduced into them in the manner described, oxygen being introduced subsequently by means of this "elec-

* H. E. Ives and A. R. Olpin, *Phys. Rev.* (2), **34**, No. 1, 117–28 (1929).

† N. R. Campbell, *Phil. Mag.* (7), **6**, 933 (1928).

‡ P. Selényi, *Ann. d. Phys.* (4), **84**, 111 (1927); **85**, 643 (1928).

trolysis in the reverse direction." As the formation of oxygen likewise takes place according to Faraday's law, the quantity of oxygen introduced can be chosen at will, as long as a certain upper limit is not exceeded. This upper limit—amounting to about 2 milliampere minutes per square centimetre of glass surface—is determined by the fact that in the case of this "reversed electrolysis" the well-known layer of SiO_2, which is a bad conductor of electricity, is formed on the inner glass wall, and the intensity of the current passing through is gradually reduced to zero.

The effect of the oxygen introduced is also noticeable in the external appearance of the cell; the silvery white colour of the sodium surface gradually passes into a colour between reddish yellow and bluish violet. The further behaviour of cells with oxidised sodium cathodes is quite similar to that of cathodes treated with nickel, only the process of activation and dis-activation takes place here at a rate

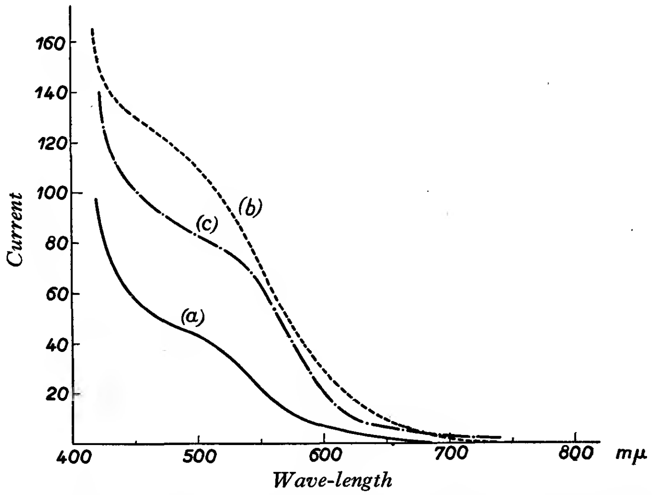


Fig. 8. Curves of spectral sensitiveness of oxidised sodium cathodes: (*a*) immediately after treatment; (*b*) 1 day after treatment; (*c*) 4 days after treatment.

many times slower. This may perhaps be explained by the fact that in the presence of oxygen there exists no clean, unoxidised sodium surface; the gradual covering-up of the oxide layer with atoms of sodium can therefore occur in this case by means of diffusion through the oxide layer only. This fits in very well with the fact that the more oxygen has been introduced, the longer will be the time during which the cells remain "active." In general the sensitiveness toward red will not disappear earlier than in 3 to 4 months, in the case of some cells at an even slower rate; the total sensitiveness, which in the most favourable case amounts to from 6 to 8 times that of a pure sodium cathode, is also reduced simultaneously by from 30 to 50 per cent. Table 3 and curves (*a*), (*b*), and (*c*) in Fig. 8 illustrate the behaviour of an oxidised cell of this type (No. K 15).

The form of the curve of spectral sensitiveness is—as may be seen—entirely similar to that of the cells treated with nickel; in the neighbourhood of 500 mμ (in other cases nearer 450 mμ) a secondary maximum is formed and the long-wave

limit is shifted to about 800 mμ. It is very interesting to note that this secondary maximum seems to be characteristic for all kinds of activation, and not only for sodium but also for potassium. Thus the same maximum in the distribution curve is presented by the Campbell "potassium-on-copper" cells of the General Electric Company, London, as by the cells treated with water vapour, sulphur, benzene, etc. by Olpin*. It should be remarked finally that the spectral distribution curve of oxidised cells of this kind remains displaced toward red to some extent even after a year, when they are no longer sensitive toward red, and that the maximum referred to remains clearly defined even after such a lapse of time (see Fig. 4, curve (*b*)). For these reasons these cells are, even in the condition referred to, more suitable, for instance, for photometric purposes than the so-called "hydrated" potassium cells.

Table 3. Variation of relative sensitiveness for red with time (cell No. K 15).

Time	I_w	I_r	R per cent.	Curve in Fig. 8
Immediately after treatment	16	0·2	1·2	(*a*)
1 day	46	1·8	3·9	(*b*)
4 days	32	1·6	5	(*c*)
7 ,,	31	1·0	3·2	
12 ,,	28	1·0	3·5	
34 ,,	23	0·6	2·7	

§ 6. ON THE EMPLOYMENT OF ALTERNATING CURRENT FOR MEASURING PHOTO-ELECTRIC CURRENTS

A practice widely used at present is to arrange the cathode and anode leads of a photo-electric cell in a common socket; if in addition the leads are, as is the case with our own cells, molten into a common stem, it becomes difficult to keep the insulation resistance at a higher figure than about 10^{11} ohms. This means, however, in the case of a cell voltage of 100 volts, a dark current of 10^{-9} A, the disturbing effects of which are already felt in the case of very accurate galvanometric measurements, whilst rendering measurement by electrometer altogether impossible.

These dark currents (or, to use a more exact expression, leakages of the cell) can be rendered entirely innocuous by using an alternating current voltage as cell voltage.

In particular, the insulation resistance should be considered as being arranged as a shunt resistance R (Fig. 9) between the cathode and anode of the cell C. Now, if an alternating voltage is applied to the cell and an ordinary galvanometer G is connected in the circuit, there will flow across the latter a pure alternating current; the instrument will therefore remain at rest. If the cell is lighted up, it acts as a complete rectifier (any sensitiveness of the anode to light, if existing, can be left out of account in this connexion) and the galvanometer will indicate only the direct current flowing through it. This simple scheme will be effective in the case of dark currents (leakages) which in the case of a D.C. voltage would produce an indication

* A. R. Olpin, *Phys. Rev.* (2), **33**, 1081–2 (1929).

of many hundred scale divisions. It can, however, possibly remain of no effect if the insulating resistance is of an electrolytic nature (e.g. with moist sockets); rectifying effects may then possibly be set up and the leakage also possesses a D.C. component in the case of alternating voltage. The employment of alternating current has also been tested by us with good results in the case of the electrometric measurement of photo-electric currents. It is, indeed, impossible to use electrometers of the quartz-fibre type (single-fibre or double-fibre electrometers) as oscillations proved to be set up in the fibre under the influence of the alternating voltage, but quadrant electrometers—among others, the excellent Lindemann electrometer—can be employed with very good results. It goes without saying that the precautions usual in the case of electrometric measurements must not be neglected. If, for instance, the alternating current is taken from a distribution panel where

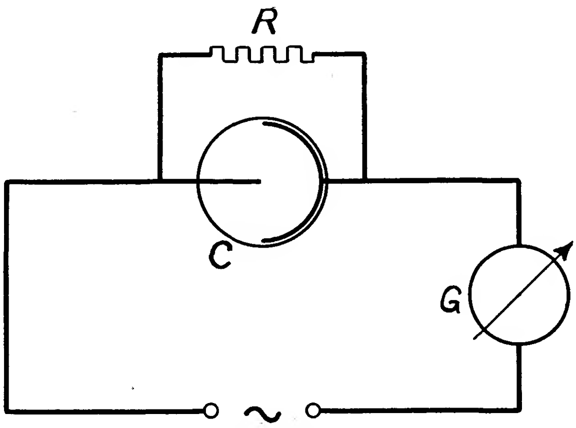


Fig. 9. Measurement of photo-electric current by means of an A.C. source and a D.C. instrument.

there is also a D.C. voltage, leakage currents of considerable magnitude are often set up. It is preferable in such a case to take the alternating voltage from the secondary coils, earthed on one pole, of a small transformer, which latter is erected in the immediate vicinity of the measuring equipment, or to ground the voltage-carrying pole immediately in front of the electrometer, for instance across a choking coil.

In connexion with alternating voltage, a most simple method of providing a compensating circuit may also be given (see Fig. 10). Two cells C_1 and C_2 are connected in parallel, with their polarities in opposition; the galvanometer G and a source of alternating current are connected to the full mains (not to any branch). As long as the illumination or the photo-electric current of both cells is the same, the same current flows through the galvanometer in both directions; if the illumination of one cell is modified, the instrument indicates the difference of intensities of illumination. This arrangement may also be used with advantage for absorption measurements, etc. Even in the case of complicated types of connexion the alternating voltage may be very useful. Thus, for instance, alternating voltage has been employed by us for a certain measurement, where the object in view was

to decide whether the intensity of the light reflected by a photo-electric cathode (sodium cathode) is altered by taking out a photo-electric current. The result was negative; as, however, the accuracy of the measurement was only 1 in 2000, nothing else could have been expected*.

The elimination of the effects of leakage currents also enables the sensitiveness of any kind of current-measuring instrument to be increased to a multiple of its original value. This possibility is based on the following line of thought. If an instrument gives a static deflection of a certain number a of scale divisions per microampere, the ballistic deflection per microcoulomb will amount to a number b of scale divisions where $b = a(\pi/t)$, t being the period of oscillation of the instrument. If, therefore, instead of measuring the photo-electric current direct by means of a galvanometer, it is allowed to accumulate in a condenser for T seconds (see Fig. 15), and this quantity of electricity is then discharged through the instrument, the ballistic deflection B obtained will be given by

$$B = bT = a\pi\,(T/t).$$

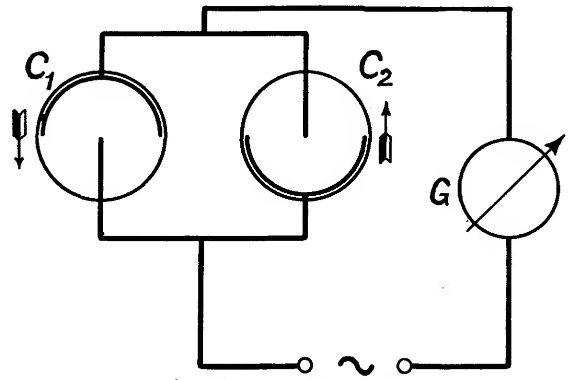


Fig. 10. Compensating connexion for alternating voltage.

A highly sensitive pointer instrument has a period of oscillation of about 3 seconds; if the period T of charging is fixed at, say, 30 seconds, B will be equal to $10a$, or, in other words, the sensitiveness of the instrument has been increased tenfold. We have often used this simple scheme with the best results. It has been possible by these means to measure intensities of illumination of a few lux units with pointer instruments; it has also been possible to take galvanometric records of the curves of spectral sensitiveness at the red end of the spectrum.

§ 7. A FEW METHODS OF CONNEXION OF LIGHT RELAYS

In the course of our work with the photo-electric cell we have found a number of methods of connexion which were novel to us; a few of these turned out later on not to be novel—for instance the method of amplifier connexion for alternating current mentioned by Campbell and Ritchie in their recently published book†.

* We shall not discuss whether a positive result is to be expected at all.

† N. R. Campbell and D. Ritchie, *Photoelectric Cells* (Sir Isaac Pitman and Sons, Ltd., 1929), p. 146.

Here we only wish to mention by way of example two methods of connexion which we have not found described in the literature.

The light relay shown in Fig. 11 possesses the characteristic feature that it reacts, independently of the general state of illumination ruling at any moment, only to the variation of the state of illumination. The method of connexion of the apparatus appears clearly from the drawing. The relay 4 to be operated is situated in the anode circuit of the thermionic valve 1; connected in parallel to these two is the photo-electric cell 5 and a large resistance 6 of a few hundred megohms, the photo-electric cell and the resistance being connected in series. The thermionic valve and the photo-electric cell are fed from the same source of current 8; the cathode of the cell is connected with the grid 2 of the thermionic valve through the condenser 7. The employment of this condenser is characteristic of this type of connexion. It is this feature notably which ensures that the grid will, independently of the illumination of the cell at any moment, always attain the same potential (approximately that of the glow-cathode) within a shorter or longer period of time

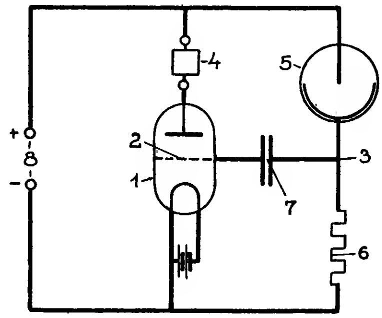


Fig. 11. Light relay independent of general illumination.

whilst the anode current will approximately possess the intensity designated as "normal anode current." By this the relay 4 is operated and keeps a current circuit closed. If now the degree of illumination of the cell is diminished, the potential of point 3 will decrease, a negative charge will be given to the grid, the anode current will be stopped, and the relay 4 will open the current circuit to be controlled. After the lapse of a certain time, the negative charge of the grid will flow out (owing to the imperfect insulation) and the former conditions will be re-established. This method of connexion can be varied in many ways. It can be arranged so as to react, contrary to the arrangement described, to the *increase* of illumination only; or it may be arranged so as to react to both increase and decrease of illumination; also alternating current may be used for this purpose instead of direct current.

Fig. 12 illustrates a light relay in which the use of thermionic valves has been entirely dispensed with, the well-known coherer having been employed instead as an amplifying element. The way the arrangement functions will be readily understood. As long as the cell is in darkness nothing happens. As soon as it is illuminated, it allows the corresponding current to pass through it, and the condenser 3 is charged until the sparking potential of the spark gap 4 is reached. At

this moment a spark flashes over, the resistance of the coherer 5 is suddenly diminished, the relay 7 is operated, and the current circuit connected to points 8 and 9 is closed. By operating a knocking device at the same time, the coherer can be restored again to its original condition of high resistance. The sensitiveness of this arrangement is indeed much smaller than that of an arrangement comprising a thermionic valve, but will probably be found sufficient for a number of purposes.

Owing to the rectifying effect of the photo-electric cell, this arrangement can be operated with alternating current just as well.

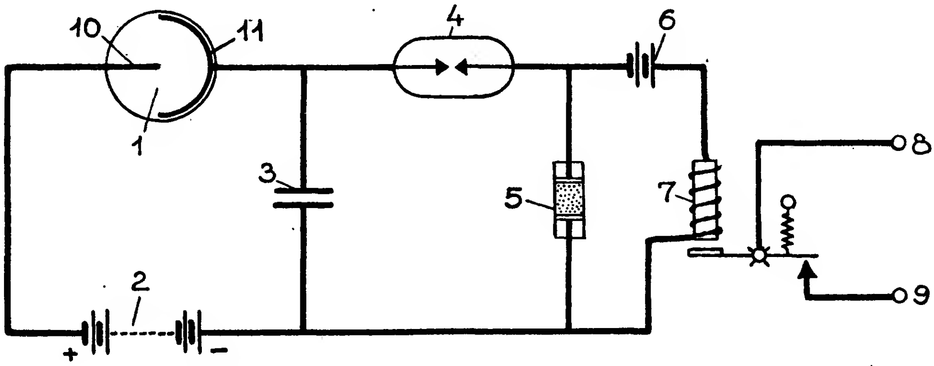


Fig. 12. Light relay functioning without amplification.

§ 8. ON THE USE OF CELLS FOR PHOTO-ELECTRIC PHOTOMETRY

As the photo-electric cells mentioned in our introductory remarks have originally been developed by us for our own use, notably for the purposes of objective photometry, we have, in the first place, been interested in their behaviour in this respect. The comparative measurements necessary for this purpose have been carried out by us in the following manner.

The light intensity of a 110-volt, 40-watt coiled filament vacuum lamp has been measured at various, widely differing voltages by the method of visual photometric observation on the one hand, and by the photo-electric method, with the aid of a number of different cells, on the other hand. The figures obtained were correlated by supposing the light intensity measured by the photo-electric method at 113·3 volts to be equal to the light intensity of 40 Hefner candles measured by the photometric method, and expressing the deviations of the other measurements as percentages. The results of such measurements have been plotted in Figs. 13 and 14, the first figure referring to the measurements effected on the vacuum lamp referred to, whilst the second refers to similar measurements carried out on a 110-volt, 40-watt gas-filled lamp. It appears from Fig. 13 that cell No. 81, possessing a pure sodium cathode, shows (curve (*a*))—owing to the want of sensitiveness towards red—a considerably lower intensity of illumination at voltages below normal and a higher intensity of illumination at voltages above normal than when measured by the visual method. In the cases of a hydrated potassium cell made by Pressler of Leipzig (curve (*e*)) and the Philips cell (curve (*f*)) the deviations are of

a similar nature, only smaller. On the other hand, cells treated with oxygen behave in an entirely different manner; in the case of cell K_{15} (curve (*c*)), the sensitiveness to red of which after having been stored for a month amounted to 3·5 per cent.,

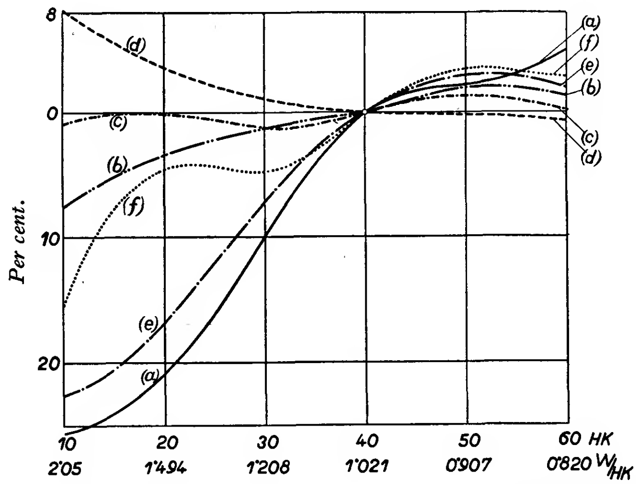


Fig. 13. Comparison of light intensities measured by photometric and photo-electric methods with various colours: (*a*) Cell No. 81, pure sodium cathode; (*b*) Cell No. 179, oxidised sodium cathode, $R=1$ per cent.; (*c*) Cell No. K 15, oxidised sodium cathode, $R=3{\cdot}3$ per cent.; (*d*) Caesium cell, General Electric Co.; (*e*) Potassium cell, made by Pressler; (*f*) Philips cell.

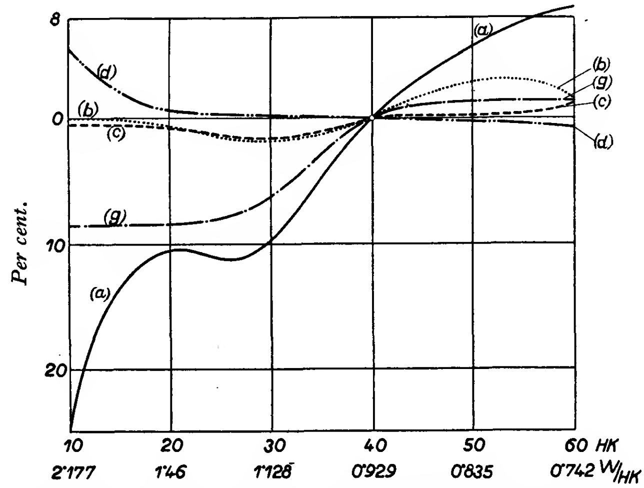


Fig. 14. Comparison of light intensities measured by photometric and photo-electric methods with various colours: (*a*), (*b*), (*c*), (*d*) as in Fig. 13; (*g*) Cell No. 189, oxidised sodium cathode, $R=0$.

the deviations from the results of measurement by the visual method are without exception within the limits of the possible errors of measurement; even cell No. 179 (curve (*b*)), possessing a sensitiveness to red of 1 per cent., hardly shows greater deviations than the caesium cell (curve (*d*)) made by the General Electric Company,

Schenectady, examined simultaneously for the purpose of comparison. The measurements effected with a 110-volt, 40-watt gas-filled lamp (see Fig. 14) show similar results. As, however, the radiation of this lamp contains less red—especially at voltages above the normal—a smaller relative sensitiveness to red is sufficient to produce these results in this case; cell No. 179, with $R = 1$ per cent. (curve (*b*)) is nearly as good as cell K_{15} with $R = 3{\cdot}3$ per cent. (curve (*c*)), and even cell No. 189, which no longer possesses any sensitiveness to red, gives results of measurement many times more favourable than those of cell No. 81, which possesses a pure sodium cathode. The caesium cell (curve (*d*)) seems to occupy an entirely privileged position in this respect, the deviations being so small as to be hardly appreciable. It should however be remarked that the visual measurements themselves did not possess a higher degree of accuracy than about 2 per cent. and when plotted did not give a completely smooth curve; if this curve were smoothed out the comparison of the various cells would result differently. In any case, the fact has been established that our oxidised sodium cells are highly suitable for objective photometry; also they attain sufficient stability after the lapse of a few weeks to make it unnecessary to check their calibration more often than, say, once a day*.

As regards the practical methods of carrying out objective photometry, the arrangement to be used should in each case conform to the purpose in view. For the purposes of checking incandescent lamps in factories in order to determine whether they are up to standard, Messrs Márton and Rostás have already described a well-designed arrangement in their paper†. Two cells, which are respectively illuminated by the standard lamp and the lamp to be measured, are arranged to influence two thermionic valves in compensated connexion; a pivoted moving-coil instrument of the usual type, possessing a small period of oscillation, will directly show the difference of candle-powers.

If it is not a question of being able to carry out measurements in very rapid succession, instruments possessing a somewhat higher period of oscillation may be used, and it is possible in this case to dispense with amplification, which means a considerably simplified arrangement as well as the elimination of possible sources of error. For the purposes of such measurements, we are using six cells connected in parallel and mounted on an Ulbricht sphere, in connexion with a suspended moving-coil instrument ($1° = 1{\cdot}4 \times 10^{-7}$ amp.); by means of a shunt, the sensitiveness of the instrument will be adjusted in such a manner as to ensure that the light intensity of the incandescent lamp to be measured can be immediately read from the scale, the divisions of the latter corresponding to candle-power units.

There exist, in addition to the above, a large number of other problems of illuminating engineering, for the purposes of which photo-electric cells are very

* Using two different cells, one with a clean sodium cathode and the other with an oxide-coated cathode, in the compensating circuit shown in Fig. 10, the resulting spectral sensitivity curve is obtained as the difference of the two single sensitivity curves (see, for instance, Fig. 4, curve (*a*) and Fig. 8, curve (*c*)). This difference-curve is nearly identical with the spectral sensitivity curve of the human eye. Combination of the two different cells must therefore lead to photometric data very nearly identical with those of visual photometry. This idea was suggested by Mr J. Frommer, of our laboratory. Some measurements recently carried out actually confirmed the above inference.

† L. Márton and E. Rostás, *loc. cit.*

convenient to use and give most satisfactory results. Thus, for instance, light distribution curves of incandescent lamps, fittings, reflectors, etc. can be ascertained by their aid in a very simple manner. To quote one example only, we have made a survey of the distribution of illumination in a room by means of photo-electric measurements. A single cell *C* (Fig. 15), fed with alternating current, is connected

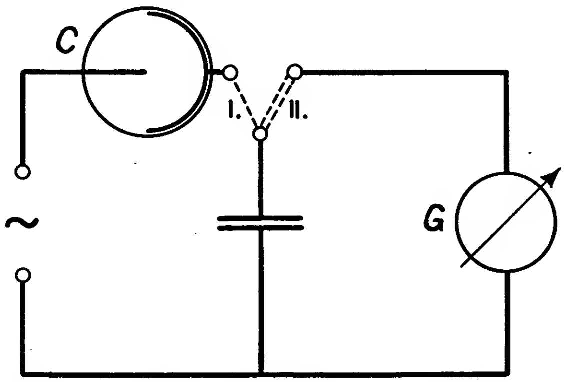


Fig. 15. Ballistic measurement of photo-electric currents.

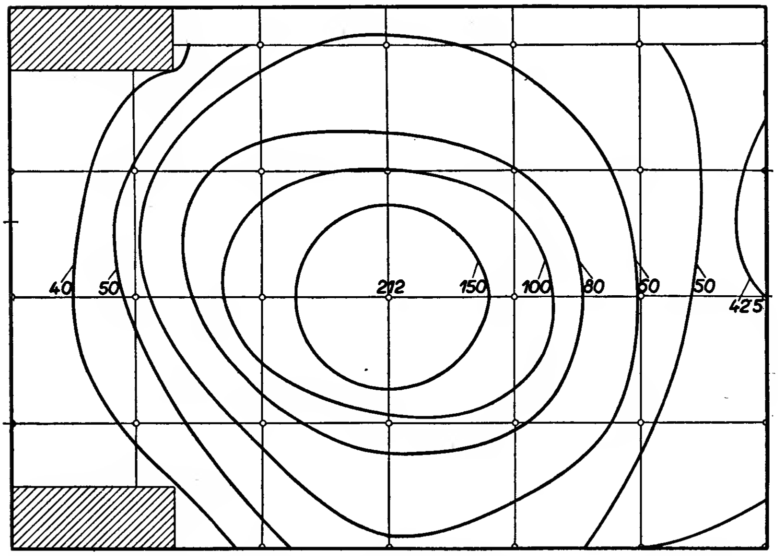


Fig. 16. Curves of equal illumination in a room lighted by a lamp in an opaque glass fitting, placed at the centre of the room.

in the way indicated and forms, in conjunction with the highly sensitive moving-coil instrument *G* referred to, a simple and most accurate illumination measuring device. A network of squares with network points of 1 m. mutual distance was traced by means of chalk on the floor of the room in question. At each point of the network the illumination was measured at a height of 1 m. above the floor and from these data the curves of equal illumination shown in Fig. 16 were plotted.

In order to eliminate errors due to variations of mains voltage, the illumination in the middle of the room was measured all the time and the figures obtained expressed as percentages of this illumination. As it is possible to place a photo-electric cell at any desired spot in space—fixed on a rod, for instance—it would be equally possible by the aid of such a cell to measure the distribution of illumination in space, and thus make an attempt to solve a number of interesting problems of illuminating engineering by these means.

Finally I would mention another instrument constructed by us recently for the measurement of reflection, transmission, and absorption of different kinds of paper, opaque glass, and similar substances. The design of this instrument is based on the well-known principle according to which the reflected as well as the transmitted quantity of light is collected in a small Ulbricht sphere and thus determined*. Six photo-electric cells, connected in parallel, have been mounted in each sphere and the quantity of light has been determined by measuring the photo-electric current. This instrument has proved itself to be most serviceable; its accuracy appears to be more than sufficient and the operation is—in contrast with visual photometric work—not tiring. We intend shortly to publish a more detailed description of this instrument and the results of measurements carried out with its aid.

It is a pleasant duty to record here the names of my fellow-workers, to whom I feel highly indebted for very valuable assistance. In working out the method of regular manufacture of our photo-electric cells, I have been greatly assisted by Mr I. Frommer, engineer; the arrangement shown in Fig. 11 and a number of different connexions, some of which have not yet been published, are his work. I also feel particularly indebted to Mr W. Rosenberg, teacher at a Secondary School, who has carried out in the capacity of a volunteer collaborator the greatest part of the measurements, requiring a great deal of time and attention, published here.

Note added later. The characteristics of the "Tungsram Nava" photo-electric cells are given in Table 4.

Table 4. Characteristics of "Tungsram Nava" cells.

Type	Cathode substance	Photo-electric current (generated by white light of gas-filled incandescent lamp)			Limits of spectral sensitivity (wave-lengths in $m\mu$)
		per lux	per lumen	100-watt lamp at distance of 6 cm.	
Nava-N	Pure sodium	$2–4 \times 10^{-10}$ A	$0{\cdot}1–0{\cdot}2 \times 10^{-6}$ A	$5–10 \times 10^{-6}$ A	From ultra-violet (350) to yellowish-green (560)
Nava-E	Oxidised sodium	$6–12 \times 10^{-10}$ A	$0{\cdot}3–0{\cdot}6 \times 10^{-6}$ A	$15–30 \times 10^{-6}$ A	From ultra-violet (350) to yellow (600) and beyond
Nava-R	Oxidised sodium	$8–16 \times 10^{-10}$ A	$0{\cdot}4–0{\cdot}8 \times 10^{-6}$ A	$20–40 \times 10^{-6}$ A	From ultra-violet (350) to red end of visible spectrum (720)

* Cp. Pirani and Schönborn, *Berichte der Fachausschüsse der deutschen Glastechnischen Gesellschaft*, Report No. 5; also I. M. Waldram, "The precise measurement of optical transmission, reflection and absorption," *Commission Internationale de l'Éclairage, Recueil des Travaux*, **6** (Sept. 1928).

THE MANUFACTURE AND USE OF THE THIN-FILM CAESIUM CELL FOR SOUND REPRODUCTION

By L. J. DAVIES, B.A., and H. R. RUFF, B.Sc.,
Engineering Laboratory, The British Thomson-Houston Co. Ltd.

MS. received June 14, 1930. *Read June* 4, 1930.

ABSTRACT. This paper describes briefly the development and production of the "Mazda" thin-film caesium cell. Curves showing the variation of sensitivity with wavelength of light are given and these, combined with other curves showing the energy radiation of lamps and the energy transmission of films, demonstrate the suitability of the caesium cell for sound reproduction.

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§ 1. INTRODUCTION

OWING to the increasing use of the sound film, the photo-electric cell now possesses industrial importance as well as scientific interest, and methods of manufacture have had to be established that will enable cells with uniform characteristics to be made in large numbers. The problems encountered in such work are somewhat different from those of a laboratory, since the efforts of the factory are concentrated on establishing schedules which will enable the production of the cell to flow smoothly and rapidly with a minimum of shrinkage due to failure in emission, or in falling outside limits previously defined. This production has to be performed, as far as possible, by non-technical labour but with skilled supervision.

The main users of the cell are Sound Reproduction Engineers, who have two main requirements that must be met. These are:

(1) The cells shall have a specified minimum sensitivity sufficient to operate the amplifier up to full output, and individual cells must not vary outside agreed limits.

(2) The sensitivity must be maintained substantially over long periods under operating conditions.

§ 2. MANUFACTURE OF CELL

The demand for cells for our own sound reproducers became sufficiently large to justify starting manufacture in the Lamp Works at Rugby. The type of cell being made is the red-sensitive, thin-film caesium type*, an illustration of the finished cell being shown in Fig. 1. An outline drawing of the cell is shown in Fig. 2. In order to facilitate production the light-sensitive surface is formed on a separate silver-plated metallic cathode rather than on the glass of the cell. While the cell is

* L. R. Koller, *Gen. Elect. Rev.* **31**, 476 (1928); *Phys. Rev.* **33**, 1082 (1929); N. R. Campbell, *Phil. Mag.* **6**, 633 (1928). We have had the advantage in the manufacture of this cell of the experience of Dr Koller and his co-workers.

being exhausted the cathode surface is oxidised and caesium formed by reduction of caesium dichromate and silicon contained in the small nickel capsule supported on the nickel rod forming the anode. The general construction of the cell is of a simple nature, consisting of the semi-cylindrical cathode at the axis of which is placed the single wire anode. These two electrodes are assembled on a single stem and sealed into a small tubular bulb. Provided sufficient care is taken in manufacture, excessive leakage current across the stem is avoided, while the use of a single stem assembly makes for rapid production. The cells are exhausted on manifolds taking six cells at a time. Operators trained in lamp and valve work are being

Fig. 1. B.T.H. "Mazda" gas-filled photo-electric cell.

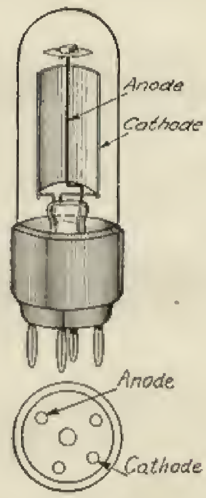

Fig. 2. Diagram of cell, with plan of base.

taught to perform the somewhat more delicate operations involved in the production of a photo-electric cell, and at present under skilled supervision are assembling, exhausting, activating, and testing cells. After tests in which the primary sensitivity and the gas amplification are recorded the cells are packed and placed in stores. They are then available for general sale, but the majority are sent without further testing to the cinema or theatre where the sound reproducing equipment is located. A small percentage of the stock is regularly withdrawn for complete testing, including life testing by the Engineering Laboratory. In addition the laboratory is responsible for the drawing up of the specifications of the cells and the design of the amplifying systems used with them. The manufacture of the cells is, therefore, now on a similar basis to that which has been used for some time with radio valves, and we feel that should the demand arise there would be little difficulty in manufacturing

larger numbers. The harsh atmosphere of the factory has enabled the somewhat delicate and wayward photo-electric cell of the laboratory to grow up into the robust and amenable article of commerce, able to stand on the same terms as the other members of the vacuum tube family, the radio valves, rectifiers, X-ray tubes and lamps, already developed.

§ 3. IMPORTANCE OF RED SENSITIVITY FOR SOUND FILM PRODUCTION

The importance of a cell sensitive to red light for sound reproduction work can be realised from the following considerations:

(1) In order to ensure correct focussing on the film, and to fit in the space available in the sound head a small tungsten filament lamp is used as the light source. To secure maximum radiation falling on the cell this filament is run at a temperature as high as possible consistent with a reasonable life. The relative energy radiated at different wave-lengths by such a source is shown approximately in Fig. 3. From this it can be seen that the greater proportion of the energy radiated is in the longer wave-lengths.

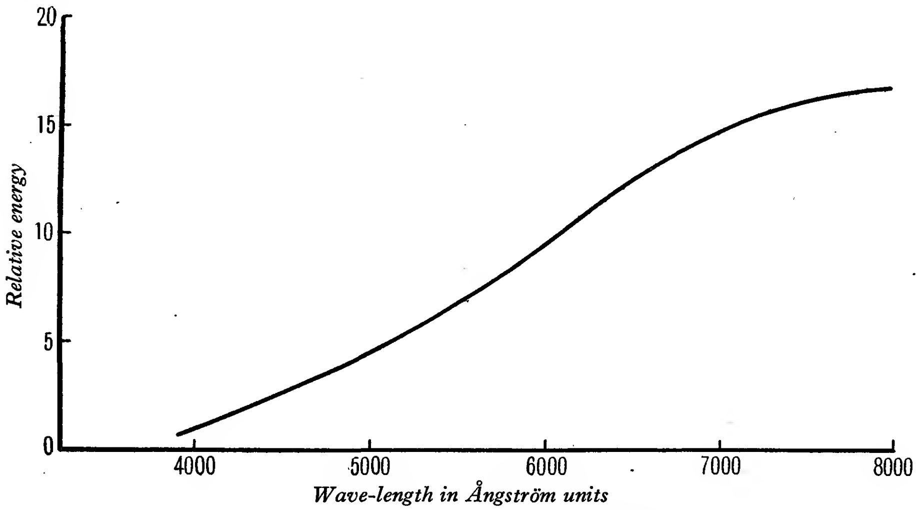

Fig. 3. Curve showing the relative energy of light of different wave-lengths emitted by a gas-filled lamp.

(2) The output of the cell is produced by the variation in light flux caused by the difference in transmission of clear and exposed film. An examination of Fig. 4 will show that with normal film the difference in transmission between clear and fully exposed film is uniform over the band of wave-lengths 4000–9000 Å., and therefore the long wave-lengths are fully effective. If the film stock is dyed, as is sometimes necessary, it will be seen that maximum difference in transmission occurs for all dyes only in the long wave-length region. Since the larger proportion of the radiation from the light source lies towards the long wave-lengths and since

it is at these wave-lengths that the maximum difference in transmission is obtained for all types of films, it is clear that the cell should respond to these wave-lengths.

The wave-length sensitivity curve of the cell at present being made is shown in Fig. 5. This curve is taken by throwing on the cell light of varying wave-length but constant energy and measuring the amount of photo-electric current produced. It will be seen that in the region 4000–8000 Å. no sharp peak occurs, whilst maximum response occurs between 7000 and 8000 Å.

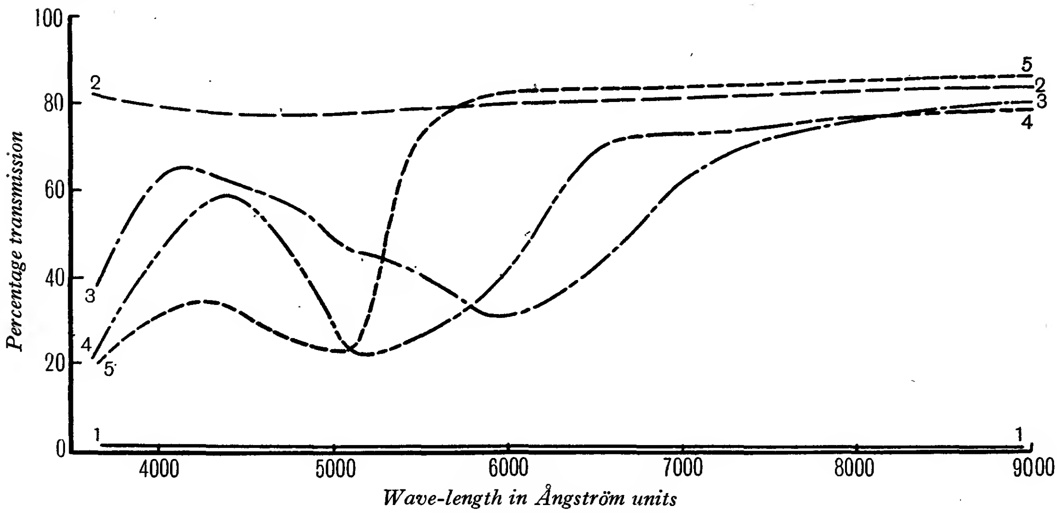

Fig. 4. Curves showing the transmission of films for light of different wave-lengths. 1. Exposed film; 2. Clear film; 3. Bluish film to represent intense daylight; 4. Film of red hue for fireside screens; 5. Light amber film to give a golden effect.

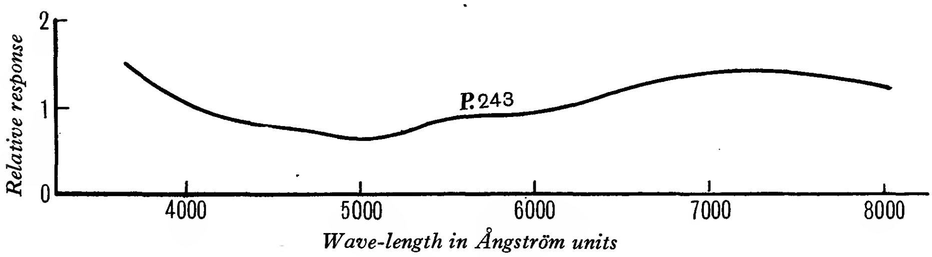

Fig. 5. Wave-length sensitivity curve for later production cells. Energy of light constant at all wave-lengths.

Fig. 6 is interesting in two ways. It shows a plot of wave-length against photo-electric response of five cells selected at random from a batch of about 200 cells, representative of early manufacture. While a certain amount of variation exists, in general the cells can be said to possess the same wave-length sensitivity curves. It will be noted, however, by comparing the average of these curves with that given in Fig. 5, that later cells have been noticeably improved as regards red sensitivity.

If the energy wave-length curve of the light source is known, the photo-electric response for any cell to this source can be calculated by multiplying the ordinates of its wave-length sensitivity curve by the corresponding ordinates of the light source curve. The response of the cell is then proportional to the area enclosed by this curve.

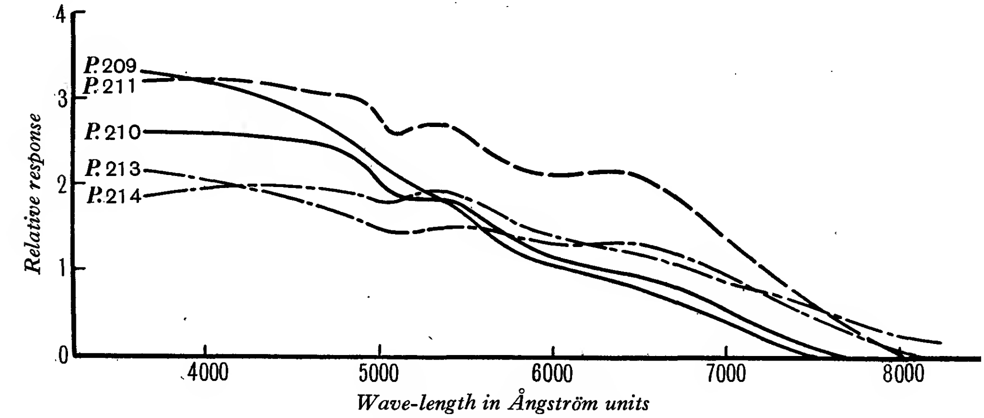

Fig. 6. Wave-length sensitivity curves for batch 1 of "Mazda" cells. Energy of light constant at all wave-lengths.

P. 211, 213, and 214 adjudged sensitive when tested with gas-filled lamp; *P.* 209 and 210 adjudged insensitive when tested with gas-filled lamp.

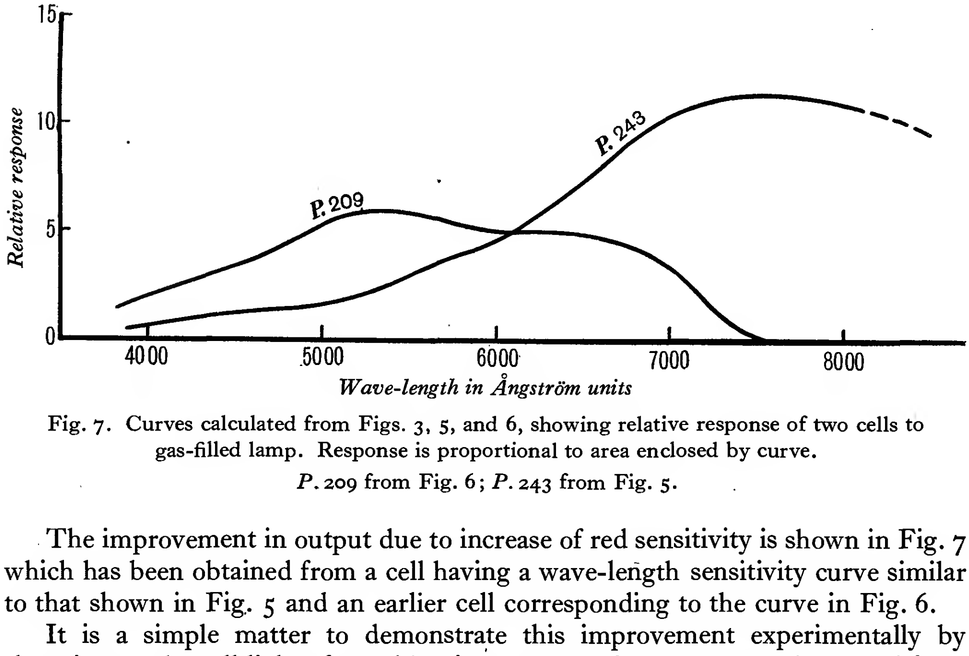

Fig. 7. Curves calculated from Figs. 3, 5, and 6, showing relative response of two cells to gas-filled lamp. Response is proportional to area enclosed by curve.

P. 209 from Fig. 6; *P.* 243 from Fig. 5.

The improvement in output due to increase of red sensitivity is shown in Fig. 7 which has been obtained from a cell having a wave-length sensitivity curve similar to that shown in Fig. 5 and an earlier cell corresponding to the curve in Fig. 6.

It is a simple matter to demonstrate this improvement experimentally by throwing on the cell light of equal luminous energy from a vacuum lamp and from a gas-filled lamp respectively. Since the eye is mainly responsive to the yellow-

green radiation, the light from the lower temperature vacuum lamp will contain a higher proportion of long wave-length radiation than the light from the higher temperature gas-filled lamp since their luminous flux has been equated. The cell having the higher red sensitivity will show a greater relative response to the vacuum lamp.

Actually, of the cells shown in Fig. 6, Nos. *P*. 209 and *P*. 210 were rejected for sound film use when tested with a gas-filled lamp, although their response to daylight would be higher than cells having curves similar to Nos. *P*. 213 and *P*. 214.

We acknowledge with thanks the co-operation we have received from the Engineering Staff of the Lamp Works in the preparation of this paper, and we have to thank the Directors of the British Thomson-Houston Co., Rugby, for permission to publish it.

BARIUM PHOTO-ELECTRIC CELLS

By THEODORE W. CASE,
Case Research Laboratory, Auburn, New York.

MS. received April 17, 1930. *Read June* 4, 1930.

ABSTRACT. Photo-electric action was discovered in Western Electric audion bulbs and the active material determined to be barium and strontium sub-oxides. This is in line with work done on other photo-electric substances such as thallium oxy-sulphide and silver sub-oxide.

The first barium cells were made with a platinum filament containing 10 per cent. rhodium. This filament was coated first with calcium oxide and then with barium oxide, and a nickel plate was used as cathode, being subsequently replaced by chemically deposited silver. Under high vacuum conditions the oxide coating on the filament is activated by an alternating current field and active material is evaporated from filament to plate.

Gas-filled cells are made by forming barium hydride by arc discharge in the cell. The correct pressure of hydrogen is determined by galvanometer readings. Four quartz gas-filled cells were made, using a similar method. Stable barium cells could not be made using lead glass. This is probably due to the fact that lead is freed by the filament activation process and has a deleterious effect.

The barium high vacuum cell is successful for daylight measurement. A high transmission yellow filter was developed to correct the response of the cell to correspond to that of the human eye. Also a shield was worked out so that the cell will follow the cosine law for the angle of incidence of impinging light. The barium hydrogen-filled cell is quite sensitive, giving approximately 98 microamperes per lumen of light flux. These gas-filled cells lose their sensitivity in the dark but regain their original action in 15 secs. upon exposure to light. There are as yet practically no data regarding the quartz cell.

Curves are given showing the effect of applied voltage on a high vacuum cell, the spectral sensitivity of the barium high vacuum cell with and without the high transmission yellow filter, the characteristics of this cell with and without the shield, and the spectral sensitivity of the hydrogen-filled cells in quartz and in glass. The spectroscopic analysis of the active surface of a barium cell in G 702-P glass is also shown.

§ 1. INTRODUCTION

THE purpose of this paper is to describe the manufacture and general characteristics of barium photo-electric cells as developed and manufactured at the Case Research Laboratory, Inc., Auburn, New York. Sufficient data are given to enable this work to be duplicated by anyone wishing to do so.

In 1920 it occurred to the writer to investigate whether there might not be an emission of negative electrons from the oxide-coated platinum filaments of Western Electric audion bulbs due solely to the influence of light rather than heat. This was first tested by inserting a potential between the plate and filament with a suitable galvanometer in series, the filament being made negative. The light from a powerful source was passed through a water bath to eliminate heat rays. This was first tried

with the filament heated and it was evident at once that photo-electric emission was present. Next, the filament when cold was exposed to the same light source and again a photo-electric action was observed. The nickel plate was made negative and an appreciably greater photo-electric current was noted.

Upon closely inspecting the nickel plates of these tubes a brownish deposit was observed, which was determined to be the active material. It was thought at first that this might be a modified structural form of either barium or strontium oxide or both, but when the tube was broken open, re-pumped, and baked, no photo-electric action could be obtained. This indicated that the active deposit had been further oxidised and consisted in its active state of either barium or strontium in the metallic form or the sub-oxides.

From the results of work done at this laboratory in 1916 and 1917, and published under the title of "The Change of Resistance of Certain Substances in Light*," it was noted that freshly prepared Ag_2O gave very appreciable light action but that after exposure to air the light action ceased; consequently it was supposed that a form of silver sub-oxide was the active element. This work led to the belief that the photo-electric action of these audion bulbs described above was not due to the pure metals but to sub-oxides, and attention is called to the fact that the so-called caesium cell at its best is caesium slightly oxidised.

During the work described in the above-mentioned article it was found that the best photo-electric action was obtained from Tl_2S, but it was again noted that a certain amount of oxidation of this material was necessary to obtain the maximum result, and the active material of the "Thalofide" cell was finally determined to be thallium slightly oxidised†. This oxidation had to be held within very narrow limits or the best results could not be obtained.

The results of practically all research done by us on light-reactive substances have pointed to the fact that a certain amount of oxidation is necessary to promote the highest response in practically all photo-electric substances which we have studied. This does not, however, include the study of selenium.

Our subsequent work on the barium and strontium cells has proved that our first deductions, in regard to the light-reactive materials on the plates of these Western Electric audions, were correct, namely, that they are sub-oxides rather than the pure metals.

§ 2. CONSTRUCTION AND METHODS OF MANUFACTURE OF THE CASE BARIUM CELLS

The first barium cells made were constructed with a platinum filament containing 10 per cent. rhodium, mounted together with a nickel plate on a glass stem. It was found necessary to incorporate 10 per cent. rhodium with the platinum so that the somewhat delicate platinum filament would stand the necessary heat without loss of shape and danger of burning out.

The filament was first heated to a dull red in air and coated with a thin layer of calcium nitrate. After a uniform coating had been obtained the filament temperature

* T. W. Case, *Phys. Rev.* 9 (2nd Ser.), 305–10 (1917).
† *Journ. Opt. Soc. Amer.* 6, No. 4, 398–406 (June 1922).

was raised to a bright red and the nitrate decomposed so that the resulting coating was calcium oxide. Immediately after this, the filament temperature was lowered to a cherry red and a very light coating of barium nitrate applied. This, in turn, was decomposed in air so that the resulting layer of barium was in the form of an oxide. Without loss of time the stem was sealed in a suitable glass bulb attached to a high vacuum pump, evacuated, and baked in the approved manner, a mercury vapour pump being used after the baking was concluded. Next, the filament was heated to a bright red and an electric field was set up between the plate and filament. In this instance it was found that the field might be alternating current of about 800 volts with approximately 150 mA. current flow. This field had the effect of heating the plate so that the necessary amount of occluded gases was expelled. The circuit was then changed over by means of suitable switches so that there was a direct current potential between plate and filament with a suitable galvanometer in series, the filament being made positive and the plate negative. Next, the filament was brought up to a bright red, a temperature which was determined by experiment, and usually after a few seconds a photo-electric effect was noted which gradually increased to a maximum, at which point the filament current was cut off and the procedure repeated.

This process we have called coating since we believe that the active barium material is formed on the filament during the previous application of the alternating current field. The active material, which may possibly contain some free barium besides the sub-oxides, has the effect of cleaning up the vacuum in the cell during this initial coating, and the second repetition of the application of the activating electrical field produces only the faintest traces of gas, and the second time the filament is heated and the direct current applied the photo-electric action is apparent almost at once and increases to a greater maximum with considerable rapidity. If the activating and coating processes are carried beyond the fourth or fifth repetition the action begins to decrease and the cell has passed its maximum point of sensitivity. We believe that this is the case because after the third or fourth time the active barium is evaporated from the filament the amount of oxygen present has been reduced to such a minute quantity that the barium which is formed on the filament during the process of activation is not partially oxidised and consequently is comparatively insensitive to light.

In regard to the barium nitrate used, we have found that it is advantageous to incorporate 0·0025 per cent. of iron and that the most uniform results can be obtained only by keeping this material in an electric drying oven at a temperature of approximately 80° C. In the preparation of this barium nitrate it is also important that it should have its final drying at a temperature not exceeding 80° C.

§ 3. RECENT METHOD OF CONSTRUCTION

The method of construction has been changed and a great many experiments on sizes, shapes, and different materials for both the plate and filament have been performed. As mentioned previously, the first cells were made with a nickel plate. Subsequently every metal that we could obtain was tested, and with some of them very good results were obtained, especially with silver. It was finally decided to

use silver evaporated on the back of the glass tube as the plate. This, however, involved a good deal of work since the silver had to be evaporated under high vacuum conditions, the tube cut open, and the stem and filament sealed in. Experiments were made with chemically deposited silver and very excellent results were obtained. It has also been found that the action of these cells was increased appreciably if the surface of the silver was slightly oxidised before the cell was pumped. This would again point to the fact that a slight amount of oxygen is necessary to produce the best response from barium.

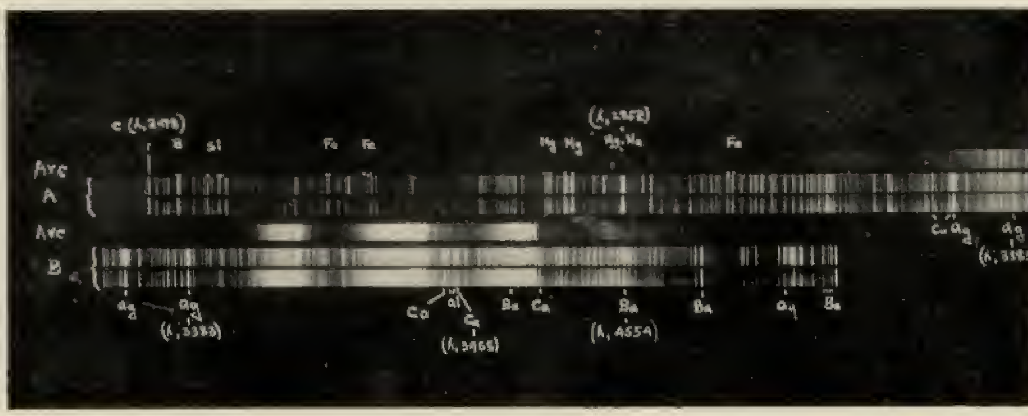

Fig. 1. Spectroscopic analysis of active coating of barium cell.

Another point which should be mentioned is that we have been unable to produce a satisfactory barium high vacuum cell using the customary lead glass with platinum or dumet wire for sealing in. A great many experiments were made with this glass and the cells would gradually lose sensitivity and after a few weeks become inoperative. Upon changing to G 702-P glass, as manufactured by the Corning Glass Works of Corning, N.Y., together with tungsten lead-in wires, the present stable cell was produced. A spectroscopic analysis of the active coating in one of these cells was made, and a high content of boron noted. This, unquestionably, comes from the G 702-P glass and probably is freed during the activation process. It is our belief that in like manner, when lead glass is used, lead is freed and has a deleterious effect upon the active barium material. The results of the spectroscopic analysis are shown in Fig. 1.

§4. PROCEDURE FOR MAKING BARIUM GAS-FILLED CELLS

The problem of making cells of the gas-filled type was undertaken and it was found that by using hydrogen of the utmost obtainable purity very remarkable results could be obtained. The method of making gas-filled cells is as follows. After the cell had been made as sensitive as possible under high vacuum conditions, a pressure of about 10 mm. of hydrogen was introduced. Then, with the filament at a dull red, an alternating current of about 650 volts was applied between the plate and filament. This ionised the gas in the cell and a discharge occurred. After arcing

in this manner for about one minute the alternating current field was cut off, the gas pumped out, and the increase in light action observed on the galvanometer. This process was repeated until no further increase in action could be obtained. At this point the operator applied a direct current potential of between 90 and 120 volts, making the filament positive and the plate negative, and, while watching the light action on the galvanometer, very small quantities of hydrogen were let into the cell until the maximum gas action was obtained. By this process we first form a barium sub-oxide which, in turn, is in whole or in part hydrided. This combination is very light-active and, upon the introduction of the correct pressure of hydrogen, 2 to 4 millimetres, an extremely sensitive gas cell results.

After many experiments it was found that pure hydrogen was the only gas that could be left in these cells. This also applies to the strontium cell and is contrary to the common practice with the alkali metals such as potassium, sodium, etc. There is one point which should be mentioned in connexion with these hydrogen-filled cells; after they have been standing without being used for a short time they will become insensitive to light. They will regain their original sensitivity, however, in from about 10 to 15 sec. upon exposure to a moderately strong light source with a potential applied. They may also be sensitised without the aid of a light source by applying a high tension current between the plate and filament for about 1 sec. This current may be supplied from any small spark coil. The desensitising of these cells is a very curious phenomenon and is not clearly understood, but we believe that it is in the nature of a chemical reaction. This desensitisation does not occur in the high vacuum cells, but only with the hydrided barium cells.

§ 5. CHARACTERISTICS OF HIGH VACUUM BARIUM CELLS

Since the high vacuum barium cell will remain constant under continued exposure to sunlight it has mainly been used for the measurement of visible daylight radiation. Also, the temperature effect is small, being less than 2 per cent. for a

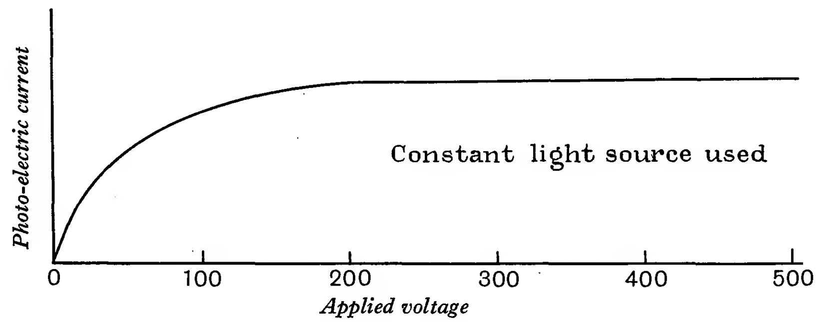

Fig. 2. Relation between applied voltage and photo-electric current in high vacuum cell.

range of from 0° to 100° F. The photo-electric current increases with increased applied potential up to about 200 volts, at which point saturation is reached and further increase in voltage produces only a very small increase in action. The relation between applied voltage and photo-electric current is shown in Fig. 2.

The maximum action of these high vacuum cells is in the blue violet, but they have considerable action in the yellow and orange. They thus lend themselves very well to the application of a special high transmission yellow glass filter so that the response of the cell will follow very closely that of the average human eye. The curves in Fig. 3 show, first, the response of the high vacuum barium cell without filter; second, that of the high vacuum barium cell with high transmission yellow filter; and third, the relative response of the average human eye.

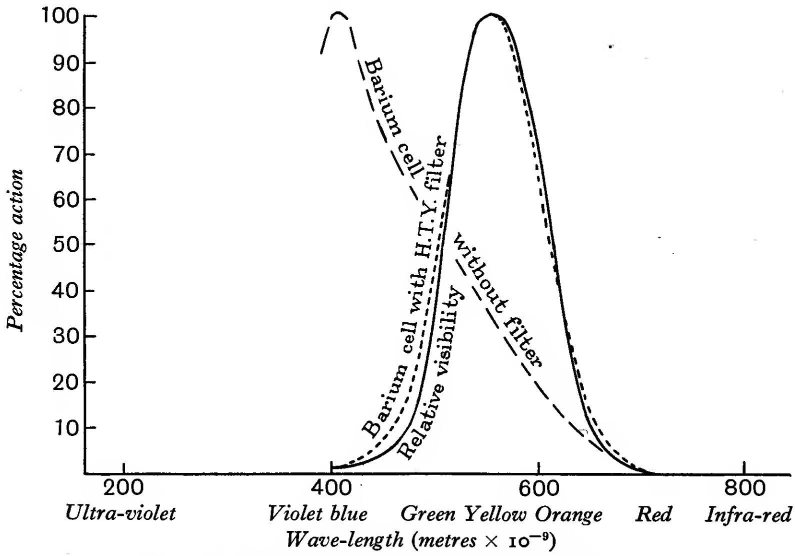

Fig. 3. Response of high vacuum cell with and without high transmission yellow filter, and relative response of average human eye.

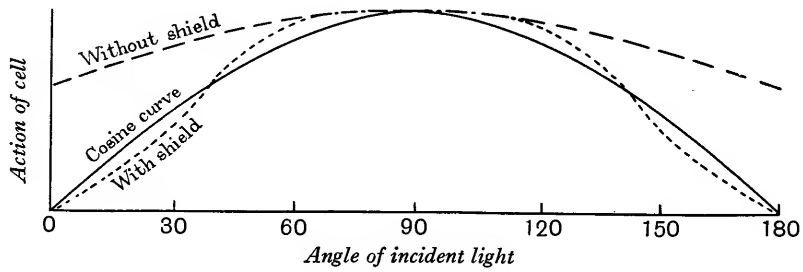

Fig. 4. Action of cell with and without shield.

To be of value for the measurement of outdoor light intensities it is necessary that the cell follow the cosine law in regard to the angle of incidence of the impinging light. In order to produce this condition it has been found necessary to place a shield on the cell. The shape of this shield was carefully worked out so that the cell functions as shown in the manner indicated in Fig. 4.

It may be added here that some of these cells have been in use for four or five years, measuring daylight and sunlight and making graphic records in conjunction

with recording potentiometers, and are giving very constant results. These high vacuum cells give a current in the neighbourhood of 300 microamperes in average sunlight.

§6. CHARACTERISTICS OF THE BARIUM GAS-FILLED CELL

As is the case with the barium high vacuum cell, the gas-filled cells will also maintain a high degree of accuracy even when exposed to bright sunlight. Of course, as is the case with all gas-filled cells, they are sensitive to changes of temperature and applied potential. The fact that they are able to stand continued exposure to sunlight

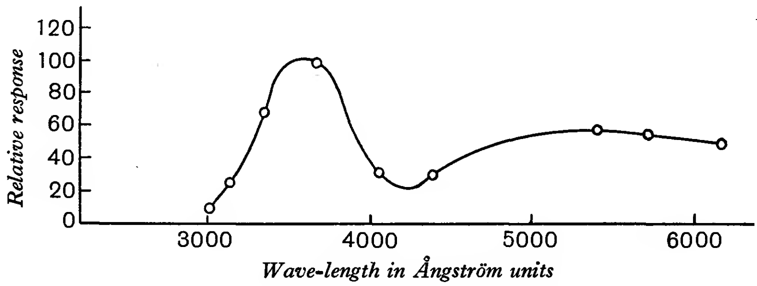

Fig. 5. Relative response of hydrogen-filled glass cell.

and the large working current which can be obtained from them are their outstanding features. Fig. 5 is a response curve for the barium gas-filled cell without filter, as worked out by the Hanovia Chemical and Manufacturing Co. A curve for this cell has not yet been made by the United States Bureau of Standards. It will be noted that the peak action has been shifted somewhat towards the red end of the spectrum.

An idea of the sensitivity of the cells may be gathered from the fact that an average of 98 microamperes per lumen of light flux was obtained from four of these gas-filled cells picked at random. The average applied voltage was about 160 volts. The cells operate nicely on this voltage with low light intensities and have proved very satisfactory for use in talking motion picture work, since their sensitivity permits the use of comparatively low amplification, with correspondingly improved quality of reproduction.

§7. THE QUARTZ GAS-FILLED BARIUM CELL

Four of these gas-filled cells have been made up in quartz but as yet we have very little data available on their life and general characteristics. A spectral curve for one of these cells is shown in Fig. 6, and it will be noted that there is a large response in the ultra-violet. It may be of interest that during the process of manufacture it was impossible to obtain much light action from the quartz cells under high vacuum conditions, but upon forming the barium hydride the response came up so that they were comparable with our best 702-P glass cells. All these quartz cells, for the short time that we had them at the laboratory, maintained their action, and the reports which we have had from those who now have them under test have been very favourable.

In conclusion, we would say that, at the present state of development, the manufacture of the barium sub-oxide cell depends considerably upon the skill and judgment of the operator. However, we believe that their stability, even under the most adverse conditions, together with their sensitivity, justifies further research.

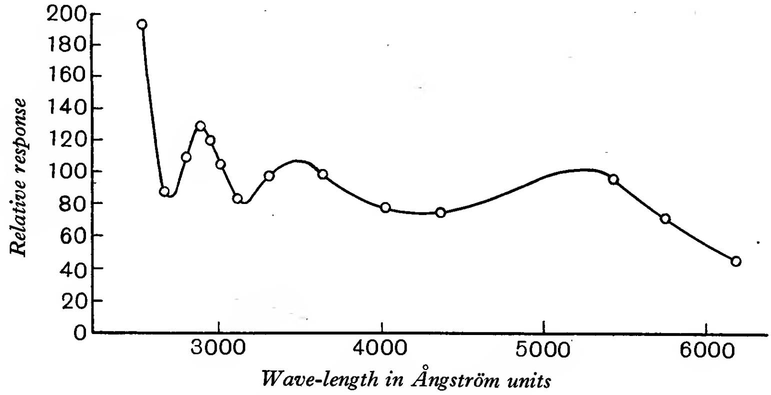

Fig. 6. Relative response of hydrogen-filled quartz cell.

THE MANUFACTURE OF PHOTO-ELECTRIC CELLS AND THEIR USE IN SOUND REPRODUCTION

By DONALD H. LOUGHRIDGE, Ph.D.,
Burt Scientific Laboratories, Pasadena, California.

MS. received April 15, 1930. *Read June* 4, 1930.

ABSTRACT. Various classes of photo-electric cells are discussed as to their basic mode of operation and reasons for the fatigue commonly present in some types of cells. The method of manufacture of a common high vacuum cell, free from fatigue, is discussed at some length as well as the gas-filled adaptation of this same type. Problems associated with the utilisation of photo-electric cells in the talking motion picture field are mentioned.

§ 1. INTRODUCTION

PHOTO-ELECTRIC cells have been for the past five decades a scientific plaything enjoyed by a few scientists in the various laboratories in the world. Elster and Geitel as far back as 1880 found that photo-electric sensitive surfaces such as potassium could be greatly increased in their response to light by "activating" with hydrogen. At that time vacuum technique was in its very infancy, and no good means were available for the production of the high vacua necessary for the preparation and storage of these extremely reactive substances which show the photo-electric effect to a high degree. Consequently results obtained by various investigators did not agree, and even a single investigator was not able to obtain reproducible results. As means and technique for obtaining smaller and smaller pressures were made available it was found that results began to be more predictable, and that a given sensitive surface began to lose a large number of its peculiar idiosyncrasies which had previously caused much trouble in interpretation.

However, it has only been within the past decade that photo-electric cells have been introduced into commercial application, and now the baby of the vacuum tube family bids fair to become one of the most robust of the group. Photo-electric cells in general may be classified into two large general groups, namely pure photo-electric and photo-voltaic. The first group is by far the more important at the present time. It can be subdivided into the sub-classes of high vacuum cells, gas-filled cells, and selenium cells, although it is doubtful whether all physicists would so classify the selenium cells. However, it is the opinion of the author, on the basis of considerable research work on the subject, that the change in resistance noticed in selenium is a secondary effect based primarily on the production of "conduction electrons" in the solid material by the action of the light, and consequently is basically the same phenomenon as occurs in the high vacuum cells. The second large classification depends upon the change in electromotive force of salt solutions,

and although this may in turn be basically the same phenomenon yet sufficient research has not been carried out to be able definitely to say so. The types which are commercially important are the high vacuum and gas-filled cells and it is the manufacture of these types with which we shall be concerned in the present paper.

§ 2. FATIGUE IN PHOTO-ELECTRIC CELLS

At the present time it is known that the great troubles experienced in the early days with photo-electric cells was due to the so-called fatigue. This phenomenon is shown in the cell when with constant illumination the current given off by the cell decreases with time. For purposes such as daylight recording, burglar alarms, measuring paper thickness, it is absolutely essential that the cell be perfectly constant. Within the last seven or eight years a great deal of work has been done in relation to this fatigue of photo-sensitive materials. The general result of this research may be formulated in the simple statement that fatigue is due to contamination of the active surface by impurities, usually in the form of gas. In a large number of the older experiments it was never possible to free entirely the active material from the gas, and consequently the upper surface was continually being bombarded by gas molecules given out from the volume of the photo-sensitive material as a whole. Under the action of light this gaseous atmosphere combines to a more or less extent with the active surface and alters its work function so that the current for a given illumination is usually caused to decrease, although with some gases the work function is lessened, and one obtains a corresponding increase in the photo-electric current. It has been one of the major problems of photo-electric cell manufacture to eliminate this fatigue as far as possible, and there have been various methods of attack. The obvious method of treatment is to obtain absolutely pure materials and keep them in a perfect vacuum. Under these conditions, and under the assumption that fatigue is due only to this contamination of the surfaces mentioned, one should obtain a perfectly stable cell. In carrying out this method some manufacturers repeatedly distil their alkali metal *in vacuo*, and by this means obtain a fairly clean surface. However, the method adopted in this Laboratory gives a greater degree of purification than is possible by mere distillation.

§ 3. METHOD OF MANUFACTURE OF BURT CELLS

Our bulbs are prepared with a filament similar to an incandescent lamp filament. In this regard they differ from any of the competing cells. The use of this filament will be apparent in a moment. The bulbs are next evacuated to better than 10^{-7} mm. of mercury, the filaments and glass being thoroughly baked out for a matter of two hours. Thus any trace of occluded gas is removed or sucked out by the pumps. Mercury vapour diffusion pumps backed up by "High Vac" oil pumps are used in this stage of manufacture. The bulbs are now sealed off from the pumps and put through an electrolytic process. The glass of which the bulbs are constructed is pure soda-lime bulb glass and consequently contains large quantities of sodium. The bulbs are placed in a small tank of water, only the upper surface where the window is to be formed being left exposed. An asbestos applicator, saturated with

sodium nitrate and kept hot by a small gas flame, is placed in contact with this exposed portion of the bulb. A D.C. potential of 150 volts is applied between the filament and this external applicator in such a direction as to draw the positive sodium ions through the glass wall. Glass is very commonly regarded as an electrical insulator, but when hot it turns out to be a very good conductor. The filament of the bulb, being lighted, furnishes a supply of electrons in the evacuated bulb and as the positive sodium ions continually appear on the inner surface of the glass wall by a process of pure ion-transfer they are neutralised and give a neutral sodium atom. This atom cannot stick to the heated glass wall above the surface of the water and so is forced to meander around until it collides with the cold glass wall immersed in the water where it sticks and the continually thickening sodium layer is deposited. Spectroscopic examination has been made of the sodium obtained in this manner from commercial sodium nitrate, and no trace of a foreign element has been detected by this most delicate method of modern analysis. Inasmuch as there can be no reaction between the metal and the high vacuum in which it is placed, these cells show a remarkable freedom from fatigue. They have actually been in use for sunlight recording year after year, being exposed to the most intense summer sun, and show absolutely no fatigue.

Modern electron theory would predict that these cells should show a saturation curve when the current is plotted against the voltage, and so they do. That is to say, under a given light intensity corresponding to a certain number of quanta per second there will be a definite number of electrons emitted, and, when the potential applied to the cell is sufficiently high, all these electrons will be attracted over to the filament which now acts as a collector. A different value of light intensity will, of course, give an entirely different saturation curve, but it is to be noted that, due to the asymptotic flatness of this curve, the voltage applied to the cell is not at all critical.

This same type of cell is made in the gas-filled form by originally sealing on to the unevacuated bulb a very small spherical container of extremely thin glass containing argon or neon in a very high state of purification. Evacuation and electrolysis are now carried out in the same manner as above indicated, and next the thin glass wall of the small container is broken by a tiny lead shot which has been sealed into the side arm holding the gas bulb. The quantity of gas has been previously adjusted to the volume of the photo-electric cell so that the final pressure will be of the order of a tenth of a millimetre of mercury. Next the side arm is sealed off the photo-electric cell bulb proper and we have a cell appearing to be the same as the high vacuum cell but with entirely different characteristics. Instead of showing saturation curves the voltage-current relations for this cell are in the form of an upturned parabola. The reason for this is the ionisation of the gas by the photo-electrons when the accelerating potential applied to the cell becomes sufficiently high to cause ionisation by collision. As the purity of the gas is made better and better the cells show an ever-increasing freedom from fatigue, but, due to the fact that present-day methods of gas purification are not all that is to be desired, it very often happens that gas-filled cells show marked fatigue, and whenever the output of a high vacuum cell is sufficiently large for the purpose at hand it is to be recommended.

§4. APPLICATION TO SOUND REPRODUCTION

Production methods have been so stabilised on the high vacuum cells that they are now nearly at the point where the three-element thermionic valve is in the matter of interchangeability. As is well known in telephonic communication circuits, it is essential that, when an amplifying tube burns out, another one identical with it be furnished so that circuit constants do not have to be altered in order to obtain the same results. It is, of course very desirable, but not essential to the same degree, to have photo-electric cells interchangeable for such uses as talking motion pictures inasmuch as the operator has at his disposal a fader (potentiometer) which controls the volume of sound so that small differences in the photo-electric cell response can be readily made up by adjustment.

Telephonic communication theory shows that for the most efficient transmission of electrical energy the impedance at any point in the communication channel should be the same in both directions. This fact requires that the impedance of the photo-electric cell be matched by the transformer or resistance to which it is coupled. Since the impedance of the photo-electric cell is of the order of a megohm, this requires a megohm matching impedance, which is impossible in the case of transformers; consequently most of the head amplifiers used in talking motion picture amplification are of the resistance coupled type. The other alternative is to produce a low impedance photo-electric cell, and a great deal of research work is being done at the present time on this problem. A further advantage of this low impedance photo-electric cell will be that it is far less subject to extraneous electrical induction effects, and consequently reduces the so-called cell noise so often prevalent in modern talking installations.

Talking motion pictures have had the inheritance of a vast field of knowledge bequeathed by the extensive radio developments of the past few years. These problems have in general been very well solved and call for only slight additional work in their adaptation to the new field. It is therefore the problems associated with the production and amplification of photo-electric currents which the new industry has to solve, and the very rapid strides in this field within the past two years have been due to the acumen and sagacity of the engineers working along these lines.

PHOTO-ELECTRIC CELLS AND SOME APPLICATIONS

By JAKOB KUNZ,
Physics Department, University of Illinois.

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ABSTRACT. In the cells described the anode consists of a ring with or without a cross of very fine wire, or in double sphere and double cylinder cells the outer glass is half-silvered and serves as anode. Recently gold-caesium cells have been constructed which show a fairly constant sensitiveness throughout the visible part of the spectrum. A new type of photo-electric valve is described.

Vacuum and gas-filled cells when properly constructed give a linear relation for light intensities varying from 1 to 100 units and in some cases from 1 to 10,000 units, i.e. to full sunlight. For very strong illumination, as, for instance, for sunlight, the cells can still give proportionality for certain, mostly low, voltages. For higher intensities than about 700 foot-candles at 85 volts the curve bends towards the abscissa, the current becoming approximately proportional to the logarithm of the illumination.

§ 1. CONSTRUCTION OF CELLS

THE photo-electric cells have been constructed with the alkali metals, lithium, sodium, potassium, rubidium, and caesium. The cells are made of ordinary glass, pyrex, or quartz. The metals are mostly distilled into the tubes, then sensitised by means of hydrogen at a pressure of about 1 mm. Hg under a potential difference of about 500 volts D.C., so that the alkali metal serves as cathode. The metal is distilled so that a desired portion of the glass surface is covered, leaving in some cases only a small window for the light to enter. The anode is made by a ring with or without a cross of very fine wire, or in double sphere and double cylinder cells the outer glass is half-silvered and serves as anode. The field between anode and cathode is as nearly uniform as possible. The dark current is decreased by making the arm bearing the anode wire as long as possible and by means of a guard-ring. After the surface has been sensitised the hydrogen is removed and sometimes replaced by a pure inert gas such as helium or argon. The sensitised surfaces show brilliant iridescent colours which vary with the metal. These colours may last for many years without change, or they may fade away in the course of time. This sensitive layer, either colloidal alkali or a hydrogen compound, is phosphorescent under the influence of ultra-violet light. The size and shape varies within wide limits. We have made cells from less than 2 cm. to about 30 cm. in diameter. The active surfaces were either simple cylinders or double cylinders, simple spheres, or collapsed spheres. Special methods had to be used for lithium cells because this metal cannot be distilled like the other alkali metals; it was therefore either dissolved in NH_3 with CH_5NH_2 and the liquid distilled away, or in recent years it was dis-

tilled by means of induced currents of high frequency. Recently gold-caesium cells have been constructed which show a fairly constant sensitiveness throughout the visible part of the spectrum.

In recent years we have found a new type of photo-electric valve. It is a glass tube about 20 cm. long and 2 cm. wide. It contains at one end an oxygen-coated filament which, when heated to a hardly visible red glow, emits a large amount of electrons; these, however, under the usual potential difference produce but a very weak current between the filament and the electrode, a silver mirror, at the other end of the tube. If now a little potassium is distilled into the cylindrical glass tube and then distilled away into the side tube, a rather large current passes between the electrodes, which is nearly proportional to the light intensity and whose sensitiveness per unit energy of incident radiation increases from the red to the violet end of the spectrum.

§ 2. CALIBRATION

The photo-electric current, varying from 10^{-14} ampere up to a few milliamperes, has been measured by different methods, involving electrometers, galvanometers, and microammeters. The simplest way of measuring currents is given by a circuit containing in series the photo-electric cell, a battery of from 20 to 200 volts, a protective resistance of at least 40,000 ohms, a switch, and a galvanometer or electrometer. For the very small light intensities and currents used in astronomy, a string electrometer of high sensitiveness is used. The rate of drift is observed. As a resistance a second photo-electric cell acted upon by a small constant light may be used. Two photo-electric cells have also been used in a Wheatstone bridge arrangement for a null method, which is exceedingly sensitive, but very delicate to handle. A very reliable method is that of equal deflection, or the current may be compensated by a second photo-electric cell which is illuminated by a constant source whose light is varied by means of a diaphragm. Photo-electric cells for scientific and practical applications require various calibrations. In the first place the characteristic curve must be determined, i.e. the relation between the current and the potential difference applied for constant light intensity. At first the current rises rapidly with applied voltage, reaches approximately a saturation value, and then for gas-filled cells increases very rapidly and the cell begins to glow, due to ionisation by collision. The saturation value of a good cell is large and nearly constant over a wide range of potential.

In the next place the relation between the light intensity and the photo-electric current has to be established for constant voltage. Empty and gas-filled photo-electric cells properly constructed give a linear relation for light intensities varying from 1 to 100 units and in some cases from 1 to 10,000 units, i.e. to full sunlight. This proportionality holds especially well for weak intensities (star light). For still weaker intensities fluctuation effects begin to appear. For very strong illumination, as for instance for sunlight, empty and gas-filled cells can still give proportionality for certain, mostly low, voltages. But here on account of space charges and reflection of electrons, marked deviations from the straight line are frequently observed; for instance, in some cells the proportionality exists up to about 700 foot-

candles for a rather high voltage of 85 volts, giving a current of about 65 micro-amperes. For higher intensities the curve bends towards the abscissa, the current becoming approximately proportional to the logarithm of the illumination. For the same cell, but for a voltage of only 65 volts, the proportionality exists through the whole range of illumination up to full sunlight. The cells are useful only in the range of voltage and light intensities in which the readings are stable and repeatable; this occurs as a rule only after some maturing process. Cells freshly made lose a part of their sensitiveness after some hours or days. Well prepared and matured and carefully treated cells maintain their sensitiveness constant for years.

The colour sensitiveness is very important. A large number of cells have been calibrated, i.e. the photo-electric current has been determined per unit energy of incident monochromatic radiation. The curves so obtained show as a rule a maximum, which is most distinct in lithium, least prominent in caesium. Sometimes two maxima have been obtained, as if the alkali metal introduced had been mixed with the alkali metal of the glass itself. One caesium cell was nearly constant between 325 and 525 $m\mu$. It is not safe to assume that a cell has a sensitivity typical of the metal with which it is made.

§ 3. AMPLIFICATION

The small photo-electric current has been amplified by means of one three-electrode tube from 100 to about 1,000,000 times. This amplification has been carried out by various circuit connexions. Amplification of small galvanometer deflections by means of the photo-electric cell has also been carried out by one of my students, Mr F. E. Null*.

* F. E. Null, "Linear amplification of galvanometer deflection by the photoelectric cell," *Journ. Opt. Soc. Amer.* **12**, 521 (1926).

TIME-LAG IN GAS-FILLED PHOTO-ELECTRIC CELLS

By N. R. CAMPBELL and L. G. STOODLEY.

(Communication from the Staff of the Research Laboratories of the General Electric Company Limited, Wembley.)

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ABSTRACT. It has often been reported that the response of gas-filled photo-electric cells, that is to say, the ratio of the amplitude of the photo-electric current to the amplitude of a varying illumination, decreases when the frequency with which the illumination varies rises above a few thousand cycles a second. Until lately the evidence has not been entirely satisfactory, because the measurements have been made with amplifiers without due attention being paid to their characteristics. But recently quite definite evidence has been produced by Metcalf; part of his results are confirmed here by experiments arranged so as to eliminate the characteristics of the amplifier entirely.

Since the same effect is not found in vacuum cells, and since it increases with the voltage applied to gas-filled cells, it must be connected with the magnification of the primary photo-electric current through ionisation. The obvious theory that the process of ionisation takes a finite time, and therefore smooths out variations in the light, appears inconsistent with calculations of the time that the process ought to take. Further evidence is produced against that theory by the discovery that the "time-lag" is not closely connected with the geometrical form of the cell.

§ 1. VACUUM AND GAS-FILLED CELLS

It is often asked whether photo-electric cells have any "time-lag." So far as vacuum cells are concerned, the answer is that they have no time-lag that arises in the photo-electric process itself. Lawrence and Beams* have shown that the interval between the incidence of light and the emission of the full quota of electrons appropriate to that light is certainly less than 10^{-8} sec.; even when the light is varying with the highest audio-frequencies there must be perfect proportionality between the rate at which electrons are being emitted at any instant and the light incident at that instant. Experiments employing amplifiers, in which the ratio of the amplitude of the output current to the amplitude of the light is measured, are less conclusive, for the influence of the electrostatic capacity of the cell is not always easily estimated. But there is no evidence† that, when vacuum cells are employed, the ratio of the amplitude of the photo-electric current to the amplitude of the light changes with frequency up to, or indeed beyond, 10,000 cycles per second.

With gas-filled cells, on the other hand, this ratio falls off notably as the frequency increases; there is something of the nature of a "time-lag," which increases with the voltage applied to the cell, and therefore with the magnification due to

* E. O. Lawrence and J. W. Beams, *Phys. Rev.* **29**, 903 (1927).

† G. F. Metcalf, *Proc. Inst. Radio Engineers*, **17**, 2064 (1929).

ionisation. But the ratio of the mean photo-electric current to the mean light does not vary; if a disc pierced with holes is interposed between the light and the cell, the current through the cell, read on a galvanometer, is totally independent of the speed of rotation of the disc, so long as it is great enough to give a steady reading. The obvious explanation is that the process of ionisation and the collection of the ions take a time comparable with the period of variation of the light; and that the current through the cell corresponds to the average value of the light during this time rather than to its instantaneous value. But, from a knowledge of the speed of the ions under an electric field and of the fields prevailing in the cell, it is possible to calculate the time that should be occupied by the ions in reaching the electrodes. This time turns out to be of the order of 10^{-5} sec.; this explanation does not seem able, therefore, to account for a variation with frequency occurring well below 10,000 cycles per second.

§ 2. PRINCIPLE OF EXPERIMENTS

In making experiments on this matter our first care was to be free of any assumptions concerning the performance of the amplifier or of the form of the variation of the light; we were determined not to assume that the amplification was linear or independent of the frequency, that the capacity of the cell was known, or that the variation of the light was harmonic. Accordingly all conclusions have been based on experiments in which the only variables on the input side were the intensity of the light beam and the voltage of the cell, these being always varied so that the average current passing through the cell was the same. We measure the relation between the mean output voltage of the amplifier and the frequency of interruption of the light, first when the light is large and the voltage on the cell small, second when the light is small and the voltage large; in the first case there is no ionisation in the cell, which is acting almost as a vacuum cell; in the second case there is much ionisation and the cell is acting as a gas-filled cell. Since the electrical circuit, interrupting mechanism, and the average photo-electric current are the same in both cases, any change in the relation between output and frequency must represent a change in the relation between the value of the light and the value of the photo-electric current at the same instant.

For let L, the illumination on the cell, be represented by

$$L = L_0 f(t)$$

and I, the current through the cell, by

$$I = I_0 F(t),$$

where L_0, I_0 are the arithmetic mean illumination and current; these means are, of course, not zero. The output voltage e is wholly determined by I; any change in the relation between e and the frequency of interruption, when I_0 is constant, must indicate a change in the function $F(t)$, that is to say, in the wave-form of the photo-electric current. But $f(t)$, the wave-form of the light, is always the same. Hence the change must mean that $F(t)$ diverges from $f(t)$ as the frequency increases, and that there is something of the nature of a time-lag.

§ 3. DESCRIPTION OF APPARATUS

The current from the cell was passed through a 200,000 ohm wire resistance connected directly to the grid and cathode of the first valve of the amplifier. Four stages were employed, the first three valves being a P. 610, H. 610, and H.L. 610 with anode resistances of 10,000 Ω, 250,000 Ω and 100,000 Ω respectively and the final stage an LS5A. The coupling was by 0·01 μF condensers and 2 megohm grid leaks. The total voltage amplification was 2500. The first three stages, together with the cell, L.T. battery, and a 100 volt H.T. dry-cell battery to supply the anode of the first valve, were enclosed in a large metal case which was earthed to prevent interference from external sources. The H.T. supply to the last three valves was obtained from external accumulators. The output was measured by an electrostatic voltmeter shunted by a 250,000 Ω resistance and connected in series with a 0·25 microfarad condenser across a resistance of 5000 Ω in the anode circuit of the last valve. While a linear response was not essential to the experiment, care was taken to ensure that each valve was working on the straight part of its characteristic.

A steel disc 12 in. in diameter and having 160 holes pierced in its circumference was used for interrupting the light. It was rotated at speeds up to 3000 r.p.m. by an electric motor and thus gave a maximum frequency of interruption of 8000 per sec. The actual frequency at any instant was determined by observing the speed of rotation with a tachometer. Light from a 24-watt lamp was projected on to the disc and after interruption was concentrated by a lens and thrown on to the cell through a small hole in the earthed case.

In taking readings, the disc was rotated slowly and absorbing gauze screens were placed between the disc and cell, to bring the output voltage as near to a given value (60 volts) as possible. The disc was then rotated at its maximum speed and allowed to slow down, simultaneously readings of output voltage and disc speed being taken. As soon as these were concluded, the cell was connected to a galvanometer and the mean current through the cell measured, first with the given voltage applied and then with 17 volts, thus giving an indication of the magnification. The average mean current used in the experiments was 0·17 microampere.

§ 4. RESULTS

The results of some typical experiments are shown in Figs. 1, 2, and 3, which refer to cells of the form shown roughly on the figures. Figs. 1 and 2 refer to spherical cells, in which the electric field was far from uniform, having cathodes respectively of sensitised potassium and a thin layer of caesium; Fig. 3 refers to a caesium cell in which the field is much more uniform. The cell of Fig. 1 was filled with argon, the others with helium. In each figure the broken line shows the relation between the R.M.S. output voltage and the frequency of interruption, when 17 volts are applied to the cell, so that ionisation is almost absent; the mean photoelectric current is about $1{\cdot}7 \times 10^{-7}$ amp. The form of this curve depends, of course, upon the capacity of the cell, the nature of the amplifier, and the intensity of the

light; these are the factors that we desire to eliminate, but the curve is useful in showing that the performance of the amplifier is not very erratic and that the amplification cannot vary very greatly with the frequency; it should also be noted that

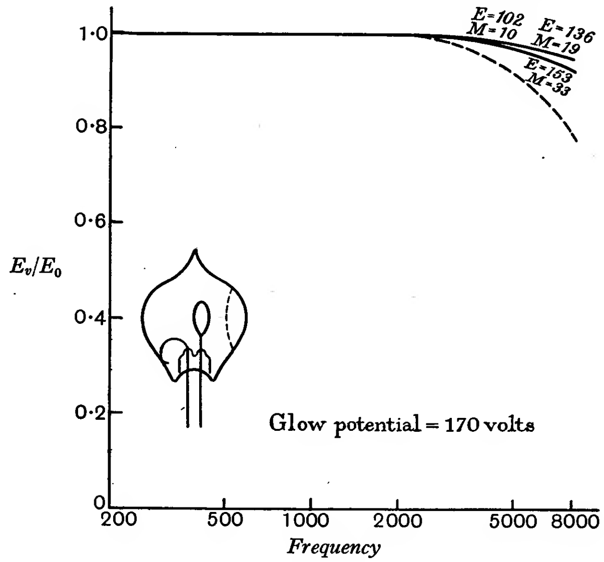

Fig. 1.

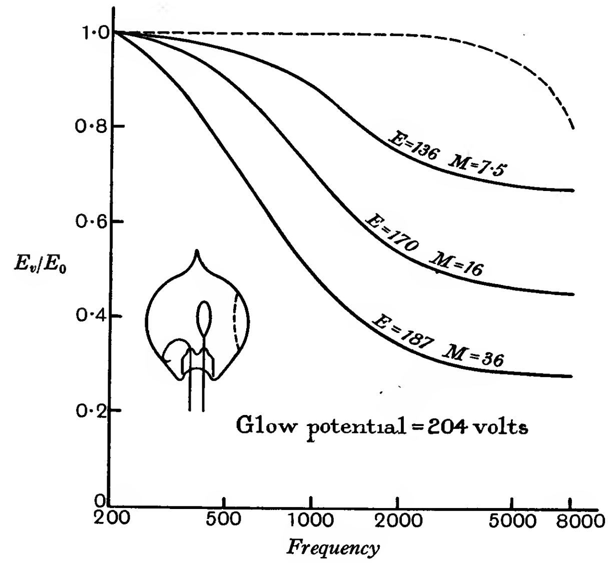

Fig. 2.

this curve varies little from cell to cell, and therefore that variations in the capacity of the cell did not affect the amplifier greatly. In the remaining full-line curves, these factors are eliminated in the manner described. The ordinates here are E_v/E_0,

where E_v is the output with voltage V on the cell and E_0 the output with 17 volts, the mean photo-electric current being always the same. (Actually it was not always exactly the same, but it was clear that a correction for small differences could be made by assuming that E_v was proportional to i.) The magnification M, i.e. the ratio of the steady current at $E_0 = V$ to the steady current at $E_0 = 17$, is marked against each curve. The fall of these curves as the frequency rises represents the apparent time-lag that we are investigating.

There is no doubt then that there is some kind of time-lag which makes the cell less effective at the higher frequencies, and that this time-lag increases in the same cell with the magnification due to ionisation. Accurate comparison of the curves for different cells would be possible if the curves for $E = 17$ were the same for all cells

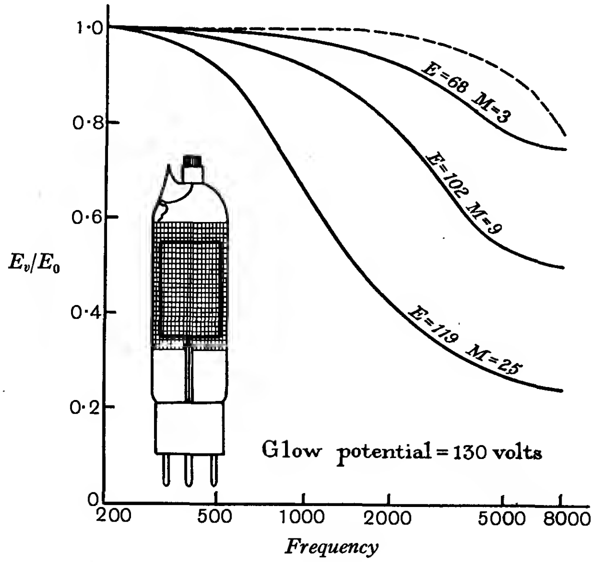

Fig. 3.

and if it were certain that this curve always represented a condition of no time-lag. These conditions are not fulfilled. Further, since the voltage-current characteristics of different cells are very different, it is not certain which curves for two cells are most appropriately compared; for instance, are we to compare the cells at the same voltage or at the same magnification? But in spite of these uncertainties the differences between the curves for certain pairs of cells are so marked, however they are compared, that it is probably legitimate to assert that one of the cells shows a greater time-lag than the other.

Interpreted in this manner, the experiments that we have already conducted establish one important conclusion. The relation between time-lag, the size of the cell, and the arrangement of the electrodes is very different from that indicated by the theory which attributes time-lag to a delay in the arrival of the ions at the electrodes. For, according to that theory, time-lag ought to be greatest in large cells with electrodes of very unequal size (e.g. the well-known spherical cell), for, in

these, ions have to travel large distances under weak electric fields. There is no evidence that the time-lag is greater in these cells than in those in which the electrodes are essentially parallel planes much nearer together; indeed we can find no clear relation between time-lag and geometrical form.

In the present state of our experiments we have no alternative theory to propose; but we hope that by the time this paper is presented to the conference we shall have additional data on which to found conclusions and shall be able to offer some explanation of the very striking differences that are found between cells of types that are in general use.

Note added later. We have continued our experiments by examining, by means of a cathode ray oscillograph, the variations of the current through the cell with the time of exposure to light. This instrument is not well suited to quantitative measurements, but it has yielded some definite conclusions.

If the light incident on the cell is caused to vary in the manner indicated by the broken line in Fig. 4, then the current through the cell varies in the manner indicated by the full line. When the light is turned on, the current rises instantaneously (or at least in a period less than 10^{-5} sec.) to h_1, and thereafter increases gradually to h_2 in a time t. When the light is turned off, the process is reversed; there is an instantaneous drop in current, followed by a slow decrease. This form of curve is general, but the ratio h_1/h_2 and the time t may vary greatly.

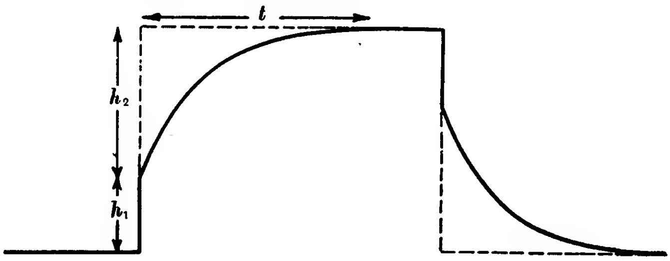

Fig. 4.

h_1 increases with the voltage applied to the cell; accordingly there is one part of the current, due to ionisation of the gas, which is subject to no time-lag, even when there is another part that is subject to great time-lag. Again the current that flows after the light is turned off compensates exactly for the current that is lost owing to time-lag; in other words, the area between the full and broken lines during the period when the light is on is exactly equal to the area between those lines when the light is off. This is proved by the fact, established by careful experiments, that the total charge passing through the cell is determined completely by the time integral of the illumination, and is totally independent of the way that the illumination varies with time.

We have not yet examined fully the variation of the ratio h_1/h_2 and the time t with the nature of the cell and the voltage applied to it, but the distortion of the wave-form resulting from the variation of these quantities depends on a combination of four factors: (1) the nature of the cathode, (2) the nature of the gas, (3) the

geometrical form of the cell, (4) the voltage applied to it. The distortion always increases with the voltage, and seems to be consistently greater with some gases than with others; thus it is always less with argon than with the other gases we have examined. But it does not vary consistently either with the nature of the cathode or with the geometrical form of the cell; thus a potassium cathode may give greater distortion than a thin-film caesium cathode in one type of cell and less distortion in another.

We have made little advance towards a theoretical explanation. Since the current continues after the light is turned off, the explanation cannot lie simply in an effect of the ion bombardment on the emission of the cathode. It appears rather that, while there is no delay in the production of electrons and ions, there is delay in the arrival of some, but not all of them, at the electrodes; but we have no suggestion to make at the moment as to how such a delay can arise.

A COMPLETE ELECTROSTATIC METHOD FOR THE MEASUREMENT OF PHOTO-ELECTRIC CURRENTS

By ERIC B. MOSS.

MS. received March 17, 1930. *Read June* 5, 1930.

ABSTRACT. The method is a null one and developed to suit the Lindemann electrometer. Improvements are incorporated which simplify both the electrical circuit and manipulation. By collecting all the auxiliary apparatus into a compact unit which is heated electrically, insulation and other errors are eliminated. The method is absolute as the actual photo-electric current is measured and widely different intensities can be determined. Either gas-filled or vacuum cells may be used.

§ 1. INTRODUCTION

THE method to be described in this paper is the outcome of attempts to obtain reliable measurements of minute light intensities with photo-electric cells which were far from perfect. The apparatus is the result of gradual improvement, but intermediate work will only be mentioned when necessary. The present technique makes it possible to take advantage of the stability of vacuum cells, the magnification obtained in gas-filled cells not being essential on account of the stability of the electrometer which results from the arrangement.

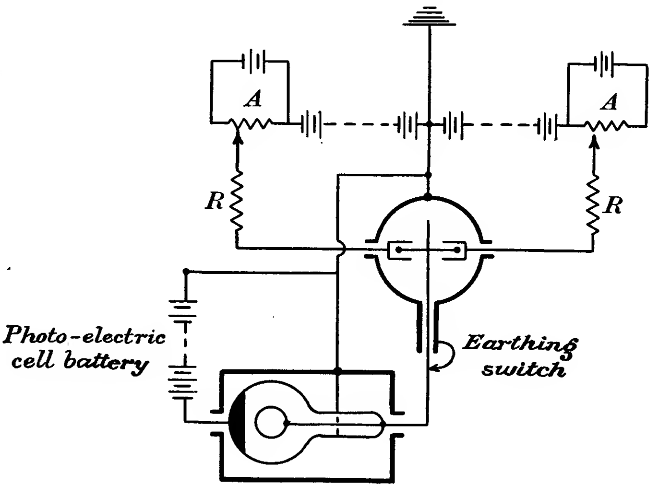

Fig. 1.

A typical circuit for the measurement of minute light intensities by a photo-electric cell in conjunction with a Lindemann electrometer is illustrated in Fig. 1. The quadrant potentials are obtained from a battery and applied through two safety resistances R, R. To earth are connected the central point of the quadrant battery,

one pole of the photo-electric cell battery, and the cell guard-ring. The method is usually comparative and the comparison is based on the times taken by the electrometer to reach a given deflection. This method has several disadvantages, although it is capable of giving accurate results under some circumstances. As far as the electrometer is concerned, the chief objections are that at high sensitivity the Lindemann electrometer has a short voltage scale and that accuracy is dependent on constant electrometer sensitivity. The objections which concern the cell are more important and will be gathered from Fig. 2. Curve *A* represents the deflection-time curve for the electrometer when the apparatus is connected as in Fig. 1 and the cell is subjected to a steady illumination, which is terminated after *t* secs. The curvature of the rising portion is due to two causes. First, as the electrometer has become

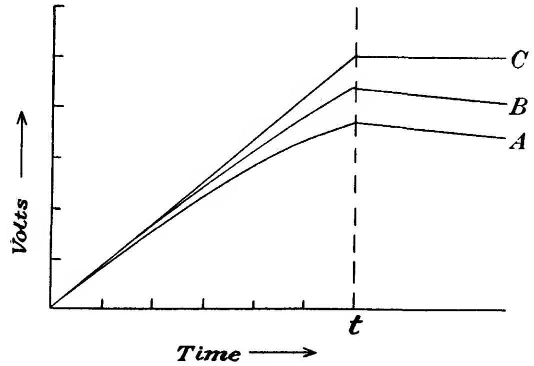

Fig. 2.

charged, the potential across the cell has gradually fallen and with it the sensitivity; second, leakage has occurred from the electrometer needle to the cell guard-ring and earth. The latter is responsible for the falling portion when the exposure had ceased.

If the circuit is so arranged that the potential applied to the cell is constant, then the deflection-time curve resembles *B* (Fig. 2), the remaining curvature being due to leakage only. A further improvement consists in altering the circuit so that the guard-ring is at the same potential as the electrometer needle and this gives a curve similar to *C* (Fig. 2).

The present method is a null one and therefore overcomes the disadvantages which were mentioned above, and are inseparable from a deflection method. At the same time, the straight deflection-time curve is obtained and errors due to leakage to the guard-ring eliminated.

§ 2. ELECTRICAL CIRCUIT

The Lindemann electrometer has been adequately described in the original paper*, but it may be of service to note here that it is a compact electrometer designed for use on the microscope stage, having small capacity and excellent insulation, and is capable of being used at any angle. The usual circuit in which it

* F. A. and A. F. Lindemann and T. C. Keeley, "A new form of electrometer," *Phil. Mag.* **47**, 578 (1924).

is connected when high sensitivity is required is shown in Fig. 1, and this arrangement can be very satisfactory. It has faults however which become apparent when attempts are made to work the electrometer for considerable periods without the possibility of checking the zero. In this circuit final adjustment of the quadrant potentials is made by two potentiometers, A, A, which must be energised by accumulators if the potentials are to be steady. It will be noted that two batteries are needed and that these may have any voltage up to 70 between them; therefore adequate insulation must be provided. Furthermore, it is possible that the batteries

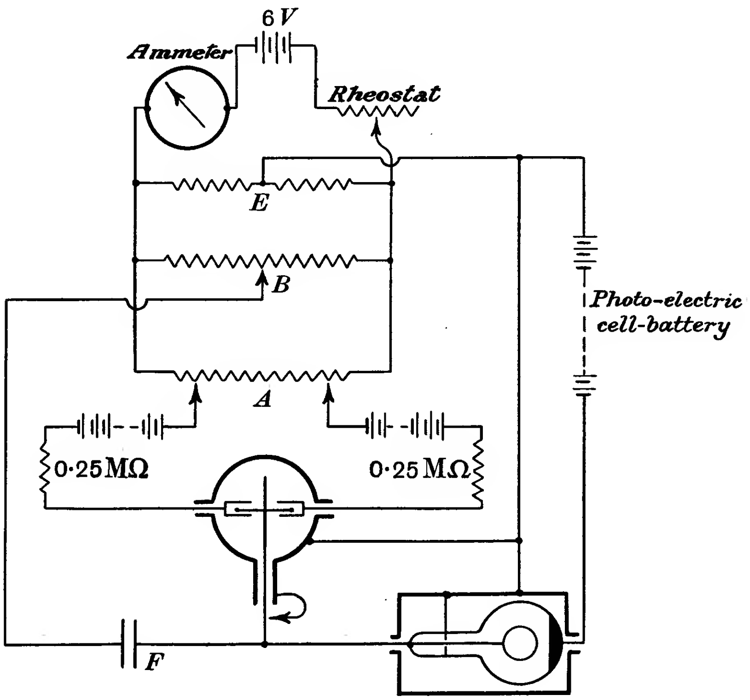

Fig. 3.

may not give a perfectly steady current and, unless the zero can be checked, steady conditions have to be assumed. A zero wander, for which the Lindemann electrometer is blamed, can often be traced to changes in quadrant potentials due to defective batteries or poor insulation.

The final circuit, shown in Fig. 3, overcomes these disadvantages by using one accumulator only, and in addition provides a complete null method, as was originally achieved by the elaboration of the circuit in Fig. 1 illustrated in Fig. 4.

The quadrant potentials are now controlled at the central point by a potentiometer A (Fig. 3) which receives its current, in common with the null-method potentiometer B, from the one accumulator. The current through all the potentiometers is controlled by a rheostat against a milliammeter, so that as long as the current is adjusted to the correct value the operator can be sure that the voltage applied to the quadrants has remained unchanged. Alternatively, the voltage across

all the potentiometers could be read instead of the current through them. The null-method potentiometer B is provided with a central zero to correspond to the earthed central point E so that either negative or positive changes in needle voltage can be measured. The additional voltages to the quadrants are supplied by two small 30 V. blocks of H.T. cells which are in themselves sufficiently insulated.

In setting up the apparatus for use the procedure is to earth the needle and quadrant terminals altogether, and to move the electrometer on the microscope stage until the image of the needle is brought to coincide with the cross-wires in the eyepiece. With the needle still earthed the quadrant potentials are raised to a value giving the required sensitivity. Throughout the process the needle is kept at the same potential as E, and as long as it is on zero this condition holds, and is a fundamental point of the method.

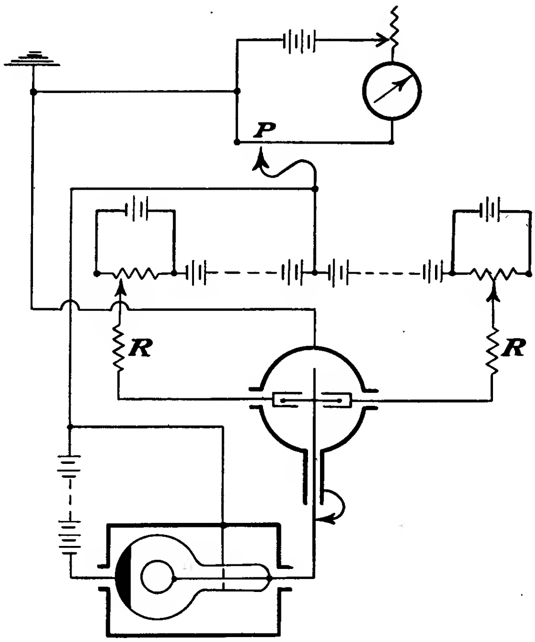

Fig. 4.

The first null-method circuit which was used is shown in Fig. 4, in which the electrometer is controlled by the circuit shown in Fig. 1. It is a fundamental characteristic of this circuit that as long as the electrometer needle is on zero it is at the same potential as the central point of the quadrant battery. Therefore, to this point are connected the guard-ring, the case of the photo-electric cell, and the positive terminal of the cell battery. A deflection of the electrometer is counteracted by moving the slider P along the potentiometer slide wire, thereby raising the potential of the whole system by an amount equal to the increase in potential of the needle. It follows, then, that the maximum potential which can exist between the needle of the electrometer and the guard-ring, thereby causing leakage, is the smallest voltage capable of detection by the electrometer. The electrometer case only is earthed;

therefore the potential measured in this way is that of the charge on the condenser formed only by the lead to the needle and the electrometer case. Capacity between the cell anode and the cell case is avoided in the final reading because, when the electrometer is balanced, the case is always at the same potential as the cell anode and needle. This capacity, however, affects the sensitivity of the apparatus. In astronomical work the cell case is mounted on the telescope and consequently earthed. Therefore, as far as Fig. 4 is concerned, point P must now be earthed and movement of the potentiometer slider changes only the potential of the electrometer case, and a balance is obtained by electrostatic induction in the condenser formed by the electrometer case and needle. The method in this respect therefore becomes similar to that published recently by N. R. Campbell and D. Ritchie*. Fig. 3 differs from Fig. 4 in the arrangement of the electrometer circuit; the electrometer case is connected to the cell case and a condenser F added to take the place of the electrometer case-needle condenser which has now been eliminated. For the greatest sensitivity the addition of this condenser is not perhaps desirable, but it has the advantage that if this capacity is known the actual photo-electric current in amperes can be calculated. The method therefore becomes absolute, not comparative.

When the electrometer is balanced, the needle must be at the same potential as the point E, and it is to this point that the cell battery is connected, so that the voltage on the cell has remained unchanged. The photo-electric current has therefore been proportional to the light intensity on the cell. If this intensity has been constant the charge on the condenser will have accumulated according to a straight line law. This results in simplification of the calculations.

Let Q = capacity of induction condenser F, in microfarads,
t = time of exposure in seconds,
V = voltage through which potentiometer slider has moved to balance electrometer.

Then photo-electric charge = VQ microcoulombs,
photo-electric current = VQ/t microamperes.

It does not matter whether point B or E is earthed; it is only a question of which plate of the condenser changes in potential.

It may be argued that to take full advantage of this method one must use a vacuum cell and that in this case constancy of potential is not important if one sufficiently high is used, but it must be remembered that high potentials tend to bring leakage troubles in their train, and by this method it is possible to use a potential that would only give 80 per cent. of saturation in the cell and yet maintain perfect accuracy even when the condenser voltage has risen to 10 per cent. of the applied voltage.

The method may be used conveniently for the measurement of large illuminations by increasing the capacity of F, and also by change of this condenser it may be used for the comparison of widely different illuminations.

* N. R. Campbell and D. Ritchie, *Photoelectric Cells* (Sir Isaac Pitman and Sons, Ltd. 1929), p. 114.

§ 3. ASSEMBLY OF THE APPARATUS

With apparatus of this kind adequate electrostatic shielding is most important, and in designing the composite instrument for this photo-electric work not only has this main point had due consideration, but also it has been necessary to bear in mind the atmospheric conditions which are encountered frequently in observatories, and to study ease of manipulation.

The complete instrument is shown in Figs. 5 and 6 and in the former are seen the eight connecting terminals. The quadrant batteries are connected to the two lower pairs, a 6 V. accumulator to the top left-hand pair, and 12 V. for the lamp to

Fig. 5.

Fig. 6.

the remaining pair. The earthing terminal is on the base. On the side of the case are the knobs for operating the various rheostats and potentiometers. The quadrant potentials are adjusted by the two lower knobs which operate two potentiometers connected in parallel that take the place of the single potentiometer A with its two sliders shown in Fig. 3. The central knob belongs to the rheostat which controls the current through the system while the large top right-hand knob moves the slider B (Fig. 3) on the main potentiometer. The remaining projection on this face is an earthing switch for the quadrants of the electrometer.

It will be noted that no external voltage scale is visible on the main potentiometer. This scale is inside, and by an optical arrangement part of it is projected into the eyepiece of the microscope which is used to view the Lindemann electrometer. The two are therefore seen together, so resulting in a great increase in ease of mani-

pulation. As the method is a null one, the electrometer needle is always kept in its zero position by adjustment of the potentiometer A (Fig. 3). The instrument is set so that, when the needle is earthed, the zero of the potentiometer scale and the needle image both coincide with the cross-wire in the microscope eyepiece. Then when the electrometer has been deflected the needle is brought back to its "zero" position by rotation of the potentiometer knob, the potential applied being read off by the position of the cross-wire on the potentiometer scale. The range of the scale is $\pm$ 2·5 V. Fig. 7 is a reproduction of what is viewed in the microscope eyepiece. The electrometer needle is seen just off zero and the potentiometer scale shows a reading of 0·3 volt. The current through the potentiometers is indicated by the milliammeter on top of the instrument; the correct value is shown by a full-scale deflection so that intermediate calibration is unnecessary. The whole case is pivoted about an axis which passes horizontally through its centre of gravity so that the

Fig. 7.

microscope can be brought to the most convenient position for observation. Fig. 6 shows that the supporting bearing is of large diameter and the shaft which goes through it, carrying the box, is a stout-walled tube through which the insulated lead is taken from the photo-electric cell. The connexion from the cell and any shielding which it may have are, therefore, undisturbed by rotation of the instrument. Near the leading-in tube is seen the needle earthing switch which is provided with a "press and turn" knob, and also a flexible shutter release so that contact can be prolonged or only momentary as desired.

Throughout the instrument vital insulation is provided by quartz but, even so, it is necessary to guard against humid conditions which are unavoidable. Drying by calcium chloride or phosphorous pentoxide was first considered, but the difficulty of making such a case as this air-tight led to the adoption of internal electrical heating. Accordingly the case is illuminated within by a 24-watt lamp, which, while providing lavish illumination, also keeps the instrument at about 25° F. above the atmospheric temperature and this has been found to keep the insulation in a satisfactory condition. The temperature inside the box is shown by the thermometer visible in Fig. 6 on the top of the instrument. A 12 V. car headlamp is used and supplied from A.C. mains through a transformer so that the lamp may be left

running continuously. The interior of the case is enamelled white and the amount of light available makes it possible to dispense with optical work for concentrating the illumination on to the electrometer, while a small mirror throws sufficient light on the potentiometer scale.

The position of the electrometer is adjusted by two knobs which project from the bottom of the case, and by rotating these the needle image may be moved as desired. Focussing of this image is carried out by rotation of the knob which is seen beside the microscope eyepiece. For gaining access to the interior of the case the side nearest to the observer is provided with a small circular aperture which is covered by a pivoted lid. Through this hole fingers can pass to adjust the position of the Lindemann electrometer, but if the hole so provided is not sufficiently large the side carrying this door can be removed as a whole, as it is only held in place by four knurled-headed screws.

The instrument has been constructed in the Research Department of the Cambridge Instrument Company, Ltd., to whom I am indebted for permission to publish this paper.

A METHOD OF COMPARING VERY SMALL AMOUNTS OF LIGHT BY MEANS OF A PHOTO-ELECTRIC CELL AND A VALVE AMPLIFIER

By G. M. B. DOBSON, M.A., D.Sc., F.R.S.,
Boar's Hill, Oxford,

AND

D. S. PERFECT, M.A., D.Phil., F.Inst.P.,
Optics Department, The National Physical Laboratory.

MS. received May 3, 1930. *Read June* 5, 1930.

ABSTRACT. The paper describes a method of comparing the relative intensities of two beams of light, and of detecting or measuring a single extremely faint beam. By means of a rotating shutter the two beams are admitted alternately to a photo-electric cell. Any difference of intensity in the beams produces a ripple in the photo-electric current which is amplified by a low-frequency amplifier. The alternating current from the amplifier is rectified by a commutator attached to the shaft of the rotating shutter, and the rectified current is measured on a microammeter or galvanometer.

§ 1. INTRODUCTION

THE method described here has been developed for comparing the relative intensities of two very faint beams of light. As a special case in which the intensity of one of the beams is reduced to zero, it can be applied to detect or measure roughly the intensity of a single beam which is extremely faint. As applied to measurements of relative intensity, faintness of the beams is not, of course, an essential condition, and the method is naturally applicable to the comparison of relatively intense beams. It is not suggested that any special point is novel, but the particular arrangement has, it is believed, not been used before, and results in an instrument capable of comparing or measuring intensities smaller than can be conveniently dealt with otherwise.

The method has been applied by us to measuring the relative intensity of two narrow bands in the spectrum*, to spectrophotometric absorption work†, and to the measurement of very small changes in angle‡. A theoretical treatment of the ampli-

* G. M. B. Dobson, "A spectrophotometer for measuring the amount of ozone in the upper atmosphere," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 185 (1930).

† D. S. Perfect, "Spectrophotometric absorption measurements," *ibid.* p. 174.

‡ D. S. Perfect, "A method of measuring small angles," *ibid.* p. 106.

fying system is dealt with in separate papers by Mr N. L. Yates-Fish* and by Mr H. A. Thomas†.

§ 2. GENERAL PRINCIPLE

The two beams of light which are to be compared are directed on to a photo-electric cell by a suitable optical system the details of which depend on the specific circumstances. A continuously revolving shutter, which may conveniently take the form of a 90° sector disc, is placed in the paths of the two beams in such a way that it permits the beams to pass alternately to the cell. The shutter is so disposed in relation to the two beams that as one beam is in course of being cut off the other is

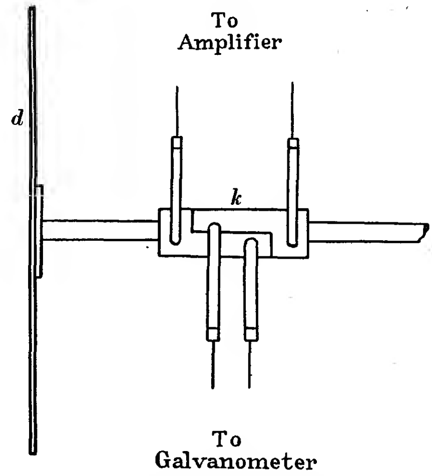

Fig. 1. Commutator and Shutter.

being uncovered, and by taking suitable precautions matters can be arranged so that if the two beams are equally intense, there is no jump in the intensity of illumination of the cell during the process of transition from one beam to the other. In these circumstances the total energy reaching the cell is constant with time, and, no matter how quick the period of the instrument used to measure the photo-electric current, no flicker would be indicated.

If, however, the intensities of the two beams are unequal, the photo-electric current will fluctuate as the shutter revolves. The fluctuations of the current are amplified by means of a low-frequency amplifier, and the amplified alternating current is rectified by means of a commutator *k* (Fig. 1) carried on the same shaft as the shutter *d*. The direct pulsating current supplied by the commutator is indicated by a suitable galvanometer (which may be replaced by a microammeter if it is desired to make the apparatus portable). By this means only such variations of current are rectified as are in phase with the rotating shutter, and the irregular variations which produce the ordinary valve noises, and become very important

* N. L. Yates-Fish, "A theoretical investigation of the use of a photo-electric cell with a valve amplifier," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 85 (1930).

† H. A. Thomas, "A theoretical study of the amplification of photo-electric currents by means of thermionic valve amplifiers," *ibid.* p. 90.

when great amplification is used, are not rectified, though, as will be seen later, they still fix the limit of sensitiveness which can be obtained. If the amplified current were rectified by a valve or metal rectifier, the irregular fluctuations would all be rectified so that the galvanometer would give a deflection for no light. If one beam be the brighter, the D.C. galvanometer in the rectified circuit will deflect one way, and if the other beam be the brighter it will deflect the other way. The brighter beam is then reduced in an accurately known ratio by some means such as an optical wedge till there is no deflection, when the two beams reaching the cell produce equal currents and are therefore equally intense. If the intensity in a single faint beam of light has to be measured, this beam is simply interrupted by the revolving shutter; the galvanometer reading is then closely proportional to the intensity of the current. A similar method has been suggested by Behr* and developed by Sharp and Kinsley†; there are also points of similarity in the equipment recently described by Hardy‡.

§ 3. ELECTRICAL SYSTEMS

The electrical systems employed by us do not differ from each other in any very essential respect. That used by one of us (G. M. B. D.) is shown in Fig. 2 and the other in Fig. 3. The photo-electric cell is connected directly to the grid of

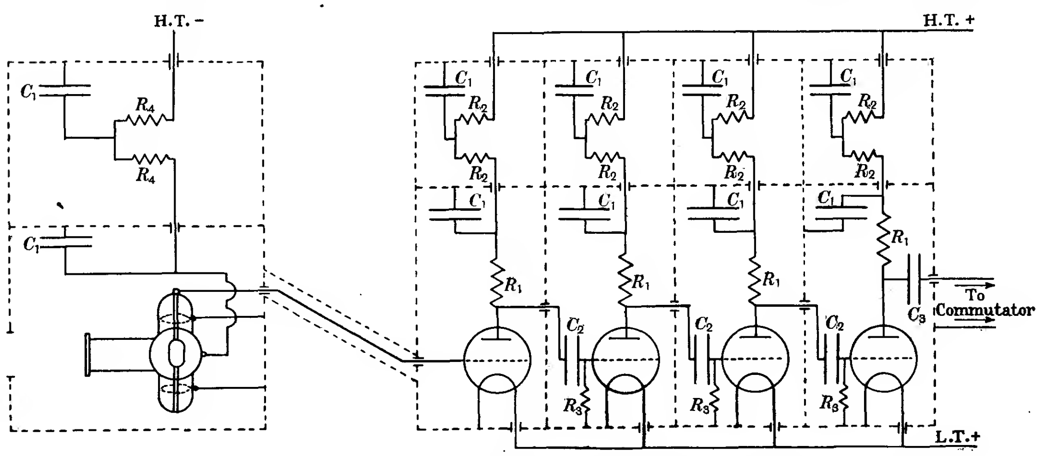

Fig. 2. Electrical system (G. M. B. D.). Broken lines indicate screening.
$C_1=2\,\mu$F; $C_2=0{\cdot}01\,\mu$F; $C_3=2\,\mu$F; $R_1=0{\cdot}1\,$MΩ; $R_2=0{\cdot}005\,$MΩ; $R_3=5\,$MΩ; $R_4=0{\cdot}1\,$MΩ.

the first valve and no grid leak is used. As the currents from the cell are very small (of the order of 10^{-12} amp.) it should make little difference whether the grid be connected to the anode or kathode of the cell, since even when connected to the anode of the cell this current can easily leave the grid owing to the ionisation of the

* Behr, "A null method of photo-electric photometry," *Minutes of Ninth Meeting of Opt. Soc. Amer.* (1924).

† Sharp and Kinsley, "A practical form of photo-electric photometer," *Trans. Illum. Eng. Soc. N.Y.* **21**, 117 (1926).

‡ Hardy, "A recording photo-electric color analyser," *Journ. Opt. Soc. Amer.* **19**, No. 2, 96 (1929).

residual gas in the valve. It is easier to obtain good insulation when the anode of the cell is connected to the grid of the valve, with the particular type of cell used, and this is probably chiefly responsible for the fact that the sensitivity obtained in practice with the grid connected to the anode was about three times that with the grid connected to the kathode.

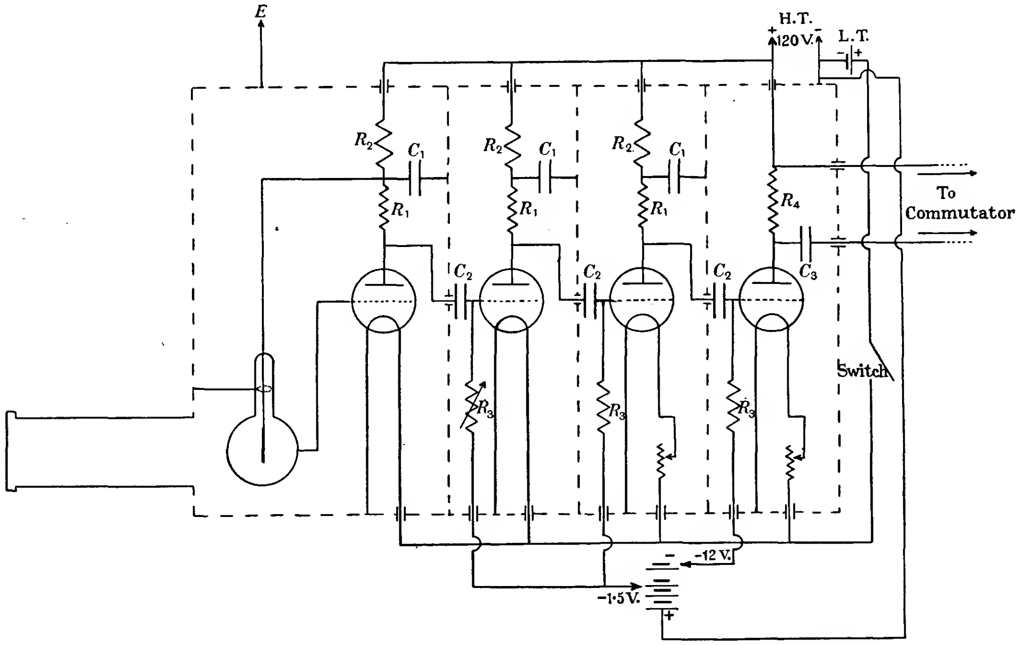

Fig. 3. Electrical system (D. S. P.). Broken lines indicate screening.
1st three valves D.E.H. 210. 4th valve P.M. 242.
$C_1=2\mu F$; $C_2=0{\cdot}01\,\mu F$; $C_3=2\mu F$; $R_1=0{\cdot}1\,M\Omega$; $R_2=0{\cdot}01\,M\Omega$; $R_3=0{\cdot}5\,M\Omega$; $R_4=0{\cdot}04\,M\Omega$.

As the amplification is very great, it is necessary to screen the amplifier very thoroughly. In one of our instruments it is built in aluminium boxes with electric filters in all the H.T. leads. We have found no difficulty in getting the amplifier perfectly stable and free from oscillation. The amount of amplification used is largely a matter of convenience, depending on the sensitivity of the galvanometer employed. The limit to the faintness of the light which can be measured is determined by the unsteadiness of the amplified current and not by the sensitivity of the galvanometer or the amplification that can be used. With the four-valve amplifier that we have used, the current cannot be read with certainty to less than 0·1 microampere owing to unsteadiness. Thus for the light to be measured to 1 per cent. it must produce a current of 10 microamperes. If greater amplification be used the current is larger, but the ratio of the unsteadiness of the current to its average value is unchanged and no greater accuracy is obtained. A like condition occurs if less amplification and a more sensitive galvanometer be used. This unsteadiness arises in the first valve, as would be expected, and if the grid of this valve be earthed either directly or through a condenser the galvanometer is perfectly steady. It is found

that if a valve with independently-heated kathode be employed the unsteadiness is rather smaller. It is also found to be a small advantage if in the coupling between valves suitable condensers to earth are added so that only frequencies are passed which are approximately equal to that of the shutter, and improvement is obtained by using a tuned circuit, adjusted to the speed of the shutter, connected across the leads from the amplifier to the commutator, to by-pass all fluctuations other than those of the same period as the shutter.

§ 4. RESULTS

To compare this method with the ordinary method of using a photo-electric cell with an electrometer, a relatively bright light was used and a Lindemann electrometer connected to the cell, the total capacity being about 30 cm. With this light the electrometer charged up at a rate of about 0·1 volt per second, so that the current from the cell was about 3×10^{-12} amp. Using the amplifier, the current was about 3×10^{-4} amp., so that the current amplification was about 10^8. Taking the limit within which readings can be made as 10^{-7} amp. for the present instrument, it follows that we can read a current to 10^{-15} amp. This is also about the limit that can be obtained with elaborate precautions when using an electrometer, but with the valve amplifier we get a direct comparison of the intensity of the two beams of light, which is what we require; and further, the relatively high frequency of alternation of the beams (of the order of 10 to 50 per sec.) enables an unsteady source of light to be used, and eliminates the effects of secular changes in the high potentials or elsewhere.

§ 5. NOTES AND PRECAUTIONS

The apparatus is naturally subject to microphonic effects. Not only the valves but especially the photo-electric cell must be carefully mounted. In one instance good results were obtained by mounting the amplifier on felt and the valves in rubber sponges; in the other the box containing the amplifier and photo-electric cell was simply mounted on rubber sponges. It must be arranged that the electrodes of the cell cannot vibrate. Naturally it is most important to see that all contacts are good and that good batteries are used for both H.T. and L.T. circuits.

At the frequency used the amplification varies approximately inversely as the capacity of the first grid, so that this should be kept small. It is shown by Yates-Fish* and by Thomas† that the amplification varies with the frequency. We have obtained satisfactory results with the shutter revolving in one case (G. M. B. D.) at a speed of 5 to 10 revolutions per second, and in the other at about twice this speed. The best setting of the brushes changes with the speed of the shutter.

With a gas-filled photo-electric cell, which must be used if great sensitivity is required, the current for a given light increases rapidly with the applied potential when this is near the arcing point. It is not possible to work very near this point, however, as a small variable current passes even when the cell is dark, which causes great fluctuations of the galvanometer. We have found a potential of some 15 volts below the arcing point satisfactory, but this may differ for each cell and is easily determined in each case.

* N. L. Yates-Fish, *loc. cit.*

† H. A. Thomas, *loc. cit.*

It is possible to replace the galvanometer by a telephone receiver. If this is done the setting of the brushes should be changed until the current is reversed at the time when it is a maximum, as this naturally gives the greatest sensitivity. The best sensitivity with telephones is, however, always less than that with a galvanometer, at the low frequencies used.

Our thanks are due to Messrs R. A. Watson-Watt, F. M. Colebrook, and H. A. Thomas for assistance with the electrical systems.

A THEORETICAL INVESTIGATION OF THE USE OF A PHOTO-ELECTRIC CELL WITH A VALVE AMPLIFIER

By N. L. YATES-FISH, B.A.

MS. received April 26, 1930. Read June 5, 1930.

ABSTRACT. A method is given of estimating the performance of a resistance-coupled amplifier at various frequencies. It is shown that a photo-electric cell illuminated by a modulated source of light is equivalent to a generator of high internal resistance, and the effect of the capacity and leakage of the first grid is then investigated. The fluctuations of the galvanometer are briefly discussed.

THE present paper gives a theoretical treatment of certain aspects of the type of detector described by Dobson and Perfect* for the measurement of small amounts of light. The theory may be conveniently dealt with in three sections: § 1. Theory of the amplifier proper. § 2. Investigation of the photo-electric cell circuit. § 3. Discussion of the irregularities which set a limit to the amount of amplification which can be usefully employed.

§ 1. THEORY OF THE AMPLIFIER PROPER

The amplifier itself is of the conventional resistance-capacity coupled type, but it may be useful to give here the main principles involved. As usually designed, the amplification is constant over a wide range of frequencies, the falling-off at low frequencies being due to the coupling condensers and that at high frequencies to the inevitable shunt capacities. At medium frequencies the amplification of each stage is given by

$$m = \frac{\mu R_e}{R_a + R_e} \qquad \text{......(1)},$$

where μ is the voltage amplification factor of the valve, R_a the anode differential resistance of the valve, and R_e the external resistance in the anode circuit. It is usual to make R_e three or four times as great as R_a, thus obtaining 75 or 80 per cent. of the theoretical maximum amplification μ; but if wire-wound resistances are used, for the sake of reliability, such high values may not be available. Using valves for which $\mu = 40$ and $R_a = 60{,}000$ ohms with anode resistances of 100,000 ohms, the amplification per stage is 25, or about 15,000 between the first and fourth grids of a four-valve amplifier.

* G. M. B. Dobson and D. S. Perfect, "A method of comparing very small amounts of light by means of a photo-electric cell and a valve amplifier," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 79 (1930).

It is important to discover at what frequencies the amplification falls away from its maximum value given by (1), and the curves of Fig. 1 enable this to be done. The low-frequency cut-off is due to the combination of series capacity (C) and shunt resistance (R) provided by the coupling condenser and grid leak, and multiplies the amplification at a frequency $\omega/2\pi$ by the factor

$$\left(1+\frac{1}{\omega^2C^2R^2}\right)^{-\frac{1}{2}}.$$

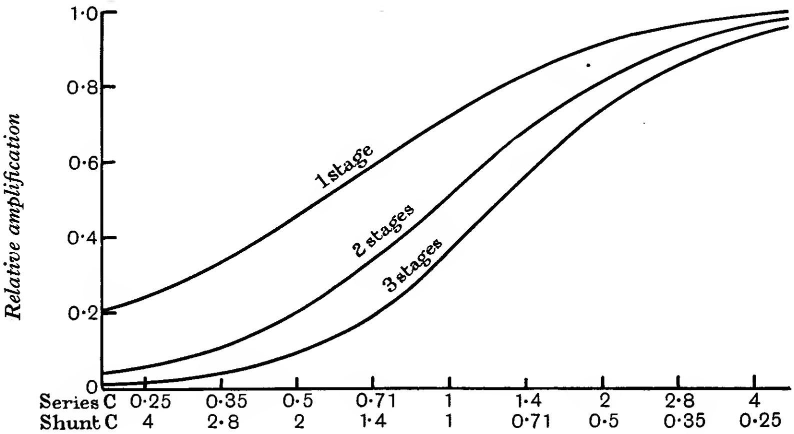

Fig. 1.

If we define the *characteristic frequency* $\omega_0/2\pi$ of such a combination by the relation

$$\omega_0 CR = 1 \qquad \text{......(2),}$$

we can express the above factor in the form

$$\left(1+\frac{\omega_0^2}{\omega^2}\right)^{-\frac{1}{2}}.$$

This is plotted in Fig. 1 against ω/ω_0, the latter on a logarithmic scale. Curves are given for one, two, and three stages of coupling.

The cut-off at high frequencies is not so easy to estimate. It is due in essence to a combination of series resistance and shunt capacity, and introduces a factor of the type

$$(1+\omega^2C^2R^2)^{-\frac{1}{2}}.$$

We may again define a characteristic frequency as in (2) and write the factor in the form

$$\left(1+\frac{\omega^2}{\omega_0^2}\right)^{-\frac{1}{2}}.$$

The curves of Fig. 1 can therefore be applied to this case by substituting for ω/ω_0 its reciprocal. Analysis shows that the appropriate value of R to use in finding ω_0 in this case is that corresponding to R_a and R_e in parallel. The effective shunt capacity is difficult to estimate, being largely due to the feed-back from plate to grid of the

succeeding valve. However, the cut-off does not become appreciable until the frequency becomes much greater than those in which we are interested in this application, unless shunt capacity is deliberately introduced, in which case its value will be sufficiently well known.

The phase changes produced in the amplifier are also important, as they affect the setting of the commutator brushes. In addition to a reversal of phase in each valve, there will be phase changes associated with the reduction of the high and low frequencies, the amount ϕ per stage being given in each case by

$$\tan\phi = \omega CR = \omega/\omega_0 \qquad \text{......(3)}.$$

This is a lag in the high-frequency case and a lead in the low-frequency case.

The current through the galvanometer due to an alternating grid voltage V on the grid of the last valve (omitting the effect of commutation) is given by

$$I = \frac{mV}{\sqrt{\left(\frac{R_a R_e}{R_a + R_e} + G\right)^2 + \left(\frac{1}{\omega C}\right)^2}} \qquad \text{......(4)},$$

where G is the resistance of the galvanometer, C is the value of the coupling condenser, and m is given by (1). If G is small and ωC large compared with

$$\frac{R_a R_e}{R_a + R_e}$$

this reduces to

$$I = \mu V/R_a.$$

§2. INVESTIGATION OF THE PHOTO-ELECTRIC CELL CIRCUIT

The current flowing through a photo-electric cell depends not only on the illumination, but also on the voltage applied to it. The behaviour of the cell can therefore be represented by a characteristic surface in a three-dimensional diagram, as in the case of the thermionic valve. We may write

$$i = f(i_0, v) \qquad \text{......(5)},$$

where i is the cell current, i_0 the "primary photo-electric emission," which is taken as a convenient measure of the effective illumination, to which it is accurately proportional, and v the voltage across the cell.

In the present application the variations of illumination and voltage are small compared with their mean values. Denoting these variations by the prefix δ, we may thus write

$$\delta i = \frac{\partial i}{\partial i_0}\delta i_0 + \frac{\partial i}{\partial v}\delta v \qquad \text{......(6)}.$$

Now the relation between the current and the terminal voltage of a generator having an internal resistance R_c and E.M.F. e_c is

$$i = \frac{e_c - v}{R_c} \qquad \text{......(7)}.$$

Comparing (6) and (7) we see that the cell used under these conditions may be regarded as a generator having an internal resistance $R_c = -\partial v/\partial i$ and an E.M.F.

$$e_c = R_c \frac{\partial i}{\partial i_0}\delta i_0 = \frac{\partial v}{\partial i_0}\delta i_0.$$

Both R_c and e_c vary with the mean voltage and mean illumination of the cell, but are independent of the impedance into which the cell delivers current.

The photo-electric cell circuit is thus essentially that of Fig. 2, in which C represents the total capacity of the cell, leads, and the grid of the first valve (including the effect of feed-back from the anode of this valve), and R_g represents the

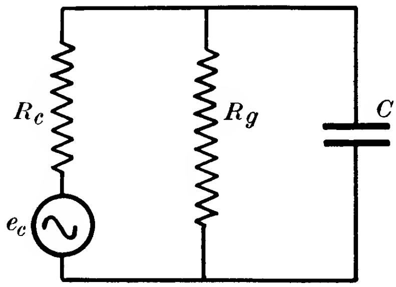

Fig. 2.

total leakage to earth of the grid, which with good insulation and in the absence of an external grid-leak is determined mainly by the slope of the grid current/grid voltage curve in the neighbourhood of zero grid current (more accurately, at the point where the grid current is equal to the mean current from the cell).

The periodic variations of the incident light can be resolved by Fourier's theorem into a number of sine components, each producing its own cell E.M.F. e_c and consequent grid voltage v_g. Alternating current theory then gives the value of the latter in vector form as

$$v_g = \frac{e_c}{1 + \frac{R_c}{R_g} + j\omega C R_c} \qquad \text{......(8),}$$

which may be put into the form

$$v_g = \frac{e_c'}{1 + j\omega C R} \qquad \text{......(9),}$$

in which $e_c' = \frac{e_c}{1 + R_c/R_g}$ and R is equivalent to R_c and R_g in parallel. The variation of response with frequency is thus identical with that shown in the upper curve of Fig. 1 used with the lower scale of ω/ω_0 for a characteristic frequency determined by substituting the values of C and R in (2). The phase lag is given by (3).

Unless the illumination is very intense R_c will be very large compared with R_g, and R may be taken as equal to R_g. The cell thus behaves as a constant-current generator under normal conditions.

To find the order of magnitude of the characteristic frequency of the grid circuit we shall assume $R = 50$ megohms, $C = 200\mu\mu\text{F}$, which give the value of about 16 cycles per second. At this frequency the response to a given light variation is 0·71 of the maximum value to which it tends as the frequency is reduced towards zero The value chosen for the capacity is much greater than would at first be expected, owing to the effect of feed-back through the capacity between anode and grid of the first valve. Although the latter is only about $5\mu\mu\text{F}$ the potential difference across it is $m + 1$ times as great as that between grid and filament, so that its effective value is magnified by this amount.

§ 3. DISCUSSION OF IRREGULARITIES

A limit is set to the sensitivity attainable with valve amplifiers by the existence of random fluctuations in the electron emission from the filaments (the Schottky or "Schrot" effect). It is clear that the irregularities which we observe are due to variations in the potential of the first grid, since they are reduced by increasing its capacity and removed by earthing it; if therefore the Schottky effect is responsible, it must operate by causing variations of the grid current about its zero mean value. The use of an independently heated cathode valve in the first stage appears to effect an improvement.

The fluctuations may presumably be regarded as being distributed over a large range of frequencies, and it seems to be desirable to limit the amplification to as narrow a frequency band as possible. The theory given above shows how this can be done in a resistance amplifier by a suitable choice of coupling components and the addition of shunt condensers between the anodes and earth.

If the impulses affecting the galvanometer are perfectly random the reversals introduced by the commutator should have no effect on them; but in practice the running of the commutator increases the unsteadiness considerably, due presumably to the discontinuities existing where the change-over takes place. A long-period galvanometer will be affected less than a quick-reading instrument, but its use would deprive the system of one of its chief advantages. It seems desirable to sacrifice the sensitivity obtained by working at very low frequencies, in order that the amplifier couplings may be designed to cut off the irregularities of long period which have the greatest effect on the galvanometer.

A THEORETICAL STUDY OF THE AMPLIFICATION OF PHOTO-ELECTRIC CURRENTS BY MEANS OF THERMIONIC VALVE AMPLIFIERS

By H. A. THOMAS, M.Sc., A.M.I.E.E.,
Wireless Division, The National Physical Laboratory.

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ABSTRACT. The paper presents a theoretical analysis of the photo-electric cell and thermionic amplifier combination when used for detecting small amounts of light. The current sensitivity is obtained together with the optimum conditions for operation. The results are applied to cases likely to arise in picture-telegraphy and television, and frequency-response characteristics are plotted for particular cases, illustrating the effects predicted from the theoretical analysis.

§ 1. INTRODUCTION

THE usual arrangement of cell and amplifier for alternating optical sources is as shown in Fig. 1. The photo-electric current passes through the high leak resistance R and produces a potential difference i_cR across it, i_c being the current in the cell. This statement is only true if the grid bias is so adjusted that no grid current flows and if the frequency of the oscillations is so low that the

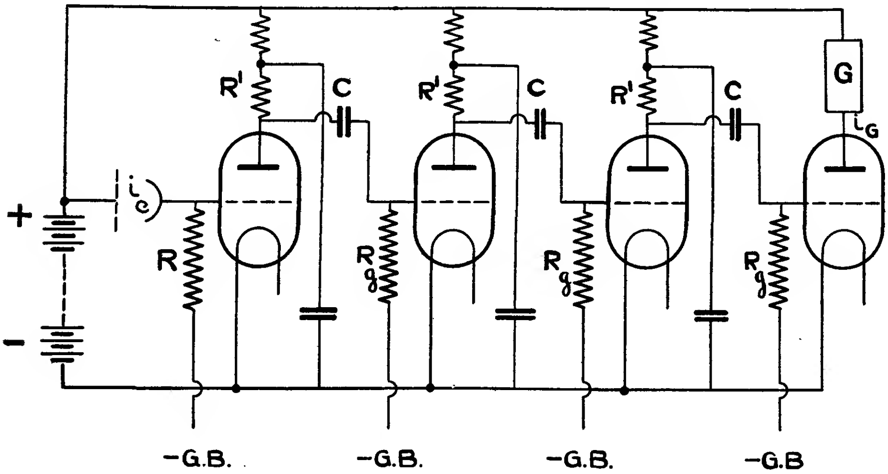

Fig. 1.

effective input impedance of the valve stage is very high compared with that of the resistance R. If the valve be so biased that the $(i_a - v_g)$ characteristic at the operating point is linear, the voltage i_cR will produce a current change gi_cR in the anode circuit where g is the mutual conductance of the valve.

The amplifier is designed to suit the frequencies required to be passed and the output voltage on the power stage grid produces a current change in this valve which operates any desired mechanism, say G (Fig. 1). The problem is to determine the ratio of the current i_G in the output mechanism to the current i_c produced in the cell due to the photo-electric effect and to determine the optimum operating conditions.

The wave form of the current i_c will follow the light fluctuations, and thus the amplifier will be supplied with waves of a complex form. For the purpose of the present analysis, we will assume that the complex wave can be expressed in terms of a number of sinusoidal terms. This may not always be true, but by analysing the behaviour of the cell and amplifier combination when excited by sinusoidal wave forms of varying frequency we obtain a reasonable knowledge of its behaviour when applied with transient and complex wave forms.

Since a general analysis has been undertaken, it was considered wise to extend the investigation to cover the properties up to frequencies of 10 kilocycles per second, representing an upper limit for television scanning and picture-telegraphy. The D.C. case with conductive coupling which gives the greatest current sensitivity can be dealt with in the general case by putting the frequency equal to zero and neglecting the effect of the coupling condensers C which are not used with conductive coupling.

We must adopt a method of analysis which proceeds back from the output stage through the amplifier to the cell. The analysis is made complex by the presence of inter-electrode capacities and their associated conductances which produce input loading effects that materially modify the performance at different frequencies.

§ 2. GENERAL ANALYSIS OF THE VALVE NETWORK

Miller* first analysed the valve network and obtained expressions for the input impedance due to the load in the anode circuit. He assumed the inter-electrode capacities to be pure, i.e. to have no associated conductance. Hartshorn† has shown that these capacities are not pure and has given a more complete analysis inserting these conductances. Colebrook‡ has recently presented the theory in a much more useful and general form, and his method of analysis and nomenclature will be adopted throughout as the mathematics is thereby considerably simplified.

The valve network has been considered by Colebrook to be representable by the diagram shown in Fig. 2. G, A, and F represent the grid, anode, and filament of the valve respectively, C_1, C_2, and C_3 the inter-electrode capacities, grid-filament, grid-anode, and anode-filament respectively, R_a the internal resistance of the valve $\frac{d\mu_a}{di_a}$, at the working point, μ the voltage factor, Z_4 the output load, and R_g the grid-filament conductivity. R_g is inserted to account for cases where grid current flows.

* Miller, *Bull. Bur. Stand.* **15**, 367 (1919).

† Hartshorn, *Proc. Phys. Soc.* **39**, 108 (1926–7).

‡ Colebrook, *Journ. Inst. Elect. Eng.* **67**, 157 (1929).

If an input e is applied in any manner, an E.M.F. μe is inserted in the anode circuit as shown in the figure, this being due to the valve characteristics. Now C_3 is in parallel with the output load Z_4 and consequently can be combined with it to form an effective output load having an admittance $Y_5' = Y_4' + Y_3'$ where Y_4' is the admittance of the load Z_4 and so equals $1/(R+jX)$, R and X being the resistance and reactance of the load Z_4 respectively, and Y_3' the admittance of the capacity C_3. So $Y_3' = j\omega C_3 + G_3$, G_3 being the conductance associated with the imperfect inter-electrode capacity C_3.

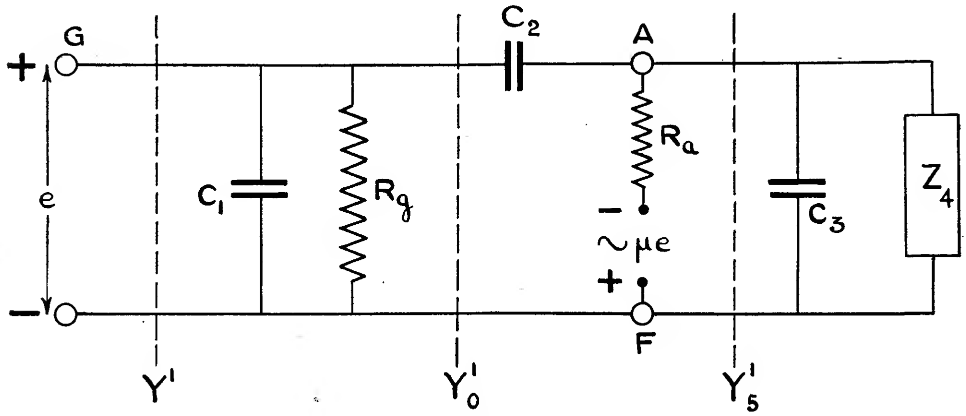

Fig. 2.

The effect of this load is to produce a net input admittance corresponding to the circuit to the right of the broken line Y_0'. This admittance

$$Y_0' = \left[\frac{(\mu+1)\,G_a + Y_5'}{G_a + Y_5' + Y_2'}\right] Y_2' \qquad \text{......(1)},$$

where $G_a = 1/R_a$, R_a being the internal resistance of the valve, and $Y_2' = j\omega C_2 + G_2$, G_2 being the conductance associated with the imperfect inter-electrode capacity C_2.

Having obtained Y_0', we can now combine this with the admittance of C_1, G_1, and G_g, G_1 being the conductance associated with the imperfect inter-electrode capacity C_1 and $G_g = 1/R_g$. From this the total input admittance Y' is given by

$$Y' = Y_0' + j\omega C_1 + G_1 + G_g \qquad \text{......(2)}.$$

This load acts as a shunt to the previous stage output circuit and modifies it accordingly. We must therefore begin with the power stage and trace its effect through each previous stage to the input.

This input admittance is very small compared with the anode circuit load at very low frequencies, but as the frequency is raised and Y_2' increased, the load becomes appreciable, thereby reducing the effective impedance of the anode circuit load in the previous stage and hence its amplification. This general effect is applicable to each stage and is most pronounced with high-voltage factor valves. Thus we shall expect a reduction in amplification at the high-frequency end of the range.

§3. THE COUPLING SYSTEM BETWEEN STAGES

With conductive coupling, the input admittance is directly added to that of the anode circuit load, but with the more usual resistance-capacity coupling this is not so at very low frequencies. The output circuit of the valve preceding the final stage can be represented as in Fig. 3, where R' is the resistance in the anode circuit

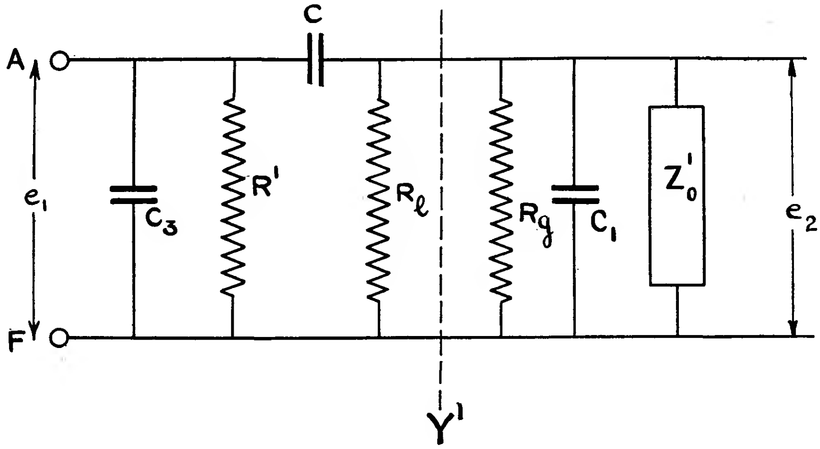

Fig. 3.

and C is the coupling condenser. R_l, R_g, C_1, and Z_0' give the net admittance $Y' + G_l$, R_l being the resistance of the grid leak, and so the total admittance of anode circuit load is

$$1\Big/\left[\frac{1}{G_l + Y'} + \frac{1}{j\omega C}\right] + \frac{1}{R'} + j\omega C_3 \qquad \text{......(3)},$$

and the ratio

$$\frac{e_2}{e_1} = \frac{Z''}{Z'' + X} \qquad \text{......(4)},$$

where

$$Z'' = \frac{1}{Y' + G_l} \quad \text{and} \quad X = \frac{1}{j\omega C}.$$

At low frequencies this ratio may be materially less than unity and represents a cut-off.

§4. THE AMPLIFIER

By the use of the expression (3), giving the load of the previous stage, we can substitute this admittance for Y_5' in equation (1) and determine the properties of the previous stage. The amplification of any stage is given by

$$m = \frac{Y_2' - \mu G_a}{G_a + Y_5' + Y_2'} \qquad \text{......(5)}.$$

The current output in the load Z_4 in the output circuit is approximately given by

$$I_4 = \frac{\mu e Z'_5}{(R_a + Z_5')\, Z_4} \qquad \text{......(6)}.$$

This expression neglects the effect of the inter-electrode admittance Y_2'. The approximation is valid in the cases with which we are dealing.

By the successive application of these expressions, the overall amplification for any number of stages can be determined and thus the ratio I_4/e_1 obtained, where e_1 is the input E.M.F. to the first grid.

§ 5. THE PHOTO-ELECTRIC CELL CIRCUIT

We require to know the ratio of e_1/i where i is the current in the cell at any frequency. The circuit diagram is shown in Fig. 4. R_l is the grid leak, $G_l = 1/R_l$, and Y' is the input admittance of the complete amplifier.

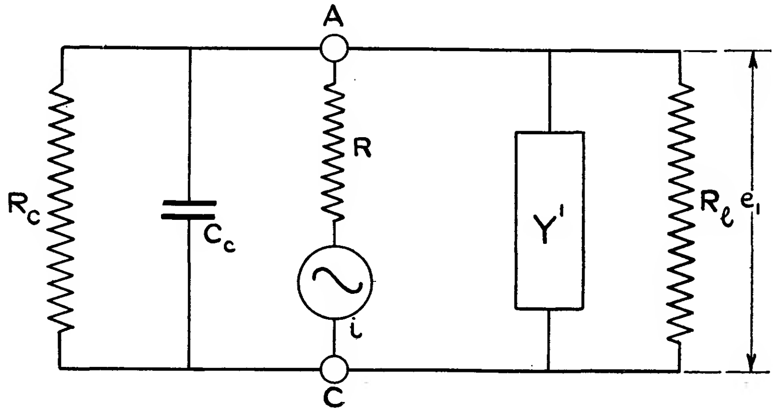

Fig. 4.

If bias is used to eliminate grid current, $Y' = Y_0' + j\omega C_1 + G_1$, but if a free grid is adopted, grid current flows and this may be represented by the term R_g. In this case the conductivity is increased by $G_g = 1/R_g$. A and C represent the anode and cathode of the cell, i is the cell current and R its internal resistance, and C_c and R_c are the cell capacity and conductance respectively. Let $Y_c = 1/R_c + j\omega C_c$, the cell admittance. Then

$$e_1 = i/(Y' + Y_c + G_l) \qquad \text{......(7).}$$

It is quite evident from this equation that for a large ratio of e_1/i we require $(Y' + Y_c + G_l)$ to be small. Both Y' and Y_c increase with frequency rise and consequently we shall get a reduced sensitivity at high frequencies. Any grid current will increase Y', producing a similar effect, but in this case with a free grid G_l is eliminated. If we desire a uniform response over a wide range of frequencies, as in television scanning, G_l must be larger than all possible values of $Y' + Y_c$. With the free grid connexion we shall increase sensitivity, but this sensitivity will be critically dependent upon frequency.

§ 6. APPLICATION TO A PRACTICAL CASE

To obtain the type of performance to be expected, we will select average values for the different constants and examine the system step by step. In all cases the values will be chosen for the worst condition likely to arise in practice. This will exaggerate the effects slightly. We will take a frequency range from 1 to 10,000

cycles per second. The output mechanism is usually a galvanometer of some form having a comparatively low resistance. Since the input impedance effect of the power stage is greatest for a large anode resistance, we will take a figure of 1000 ohms as representative of the worst case likely to arise.

Power stage

Let $Z_4 = 1000$ ohms and $C_1 = C_2 = C_3 = 10\,\mu\mu F$ (an average figure). Take the power factor of each of these as 0·05, which figure has been shown experimentally to be approximately correct. The effect of the conductances G_1, G_2, and G_3 is negligible in this case. Taking $\mu = 5$ and $G_a = 0{\cdot}2\,.\,10^{-3}$ for a typical output valve and assuming that the grid bias is sufficient to prevent grid current ($G_g = 0$), we find by applying formula (1) that $Y_0' = 10^{-6}$ at 10,000. This admittance in shunt with the grid leak R_l, which we will assume has a conductance $G_l = 0{\cdot}5\,.\,10^{-6}$, reduces its value at very high frequencies, but at these frequencies $X = 1/j\omega C$, for the coupling condenser is so low, viz. 160 ohms for $C = 0{\cdot}1\,\mu F$ (an average value), that no cut-off will take place. So we can neglect this shunting effect at high frequencies.

The current output given by equation (6) is $\frac{5}{6000}e$ or 0·83 milliamp. per volt input.

Now considering the low-frequency cut-off due to the coupling condenser, we find from equation (4) that this is

22	per cent.	at a frequency of	1	cycle per sec.
7	,,	,,	2	cycles ,,
2	,,	,,	4	,, ,,
0·1	,,	,,	10	,, ,,

The amplification of the previous stages

Now considering the amplifier to consist of stages with a valve having a factor of 20, a conductance of $50\,.\,10^{-6}$, and an anode circuit resistance of five times that of the valve, viz. $Y_5' = 10\,.\,10^{-6}$, we can determine the amplification of this previous stage. From (3) we find that the net impedance of the anode circuit load is $10{\cdot}5\,.\,10^{-6} + jY_0'$, which is $(10{\cdot}5 + j)\,10^{-6}$ at 10,000 cycles and $(10{\cdot}5 + j\,0{\cdot}1)\,10^{-6}$ at 1000 cycles, and thus the amplification given by equation (5) is 16·5. The variation with frequency is negligible. The input admittance

$$Y'_0 = j\,.\,11\,.\,10^{-10} f = j\,.\,11\,.\,10^{-6}$$

at a frequency of 10,000. This input admittance is far larger than for the power stage owing to the higher factor and higher anode resistance.

The cut-off for this previous stage given by equation (4) is similar to that for the power valve stage, and the amplification given by equation (5) is 16·2 at a frequency of 10,000 cycles per second and 16·5 at a frequency of 1000 or lower. The figures for amplification and input impedance of the previous similar stages will be substantially the same, and so we get the final characteristics shown in Fig. 5. Two curves are shown, one giving the amplification per stage of the high factor valves and the other for three such stages. Curves C refer to conductive coupling and curves R to resistance-capacity coupling.

The photo-electric cell

We now require to find the ratio of $\frac{e_1}{i} = \frac{1}{Y' + Y_c + G_l}$ from equation (7). The capacity of a typical cell was measured and found to be 4 $\mu\mu$F and the power

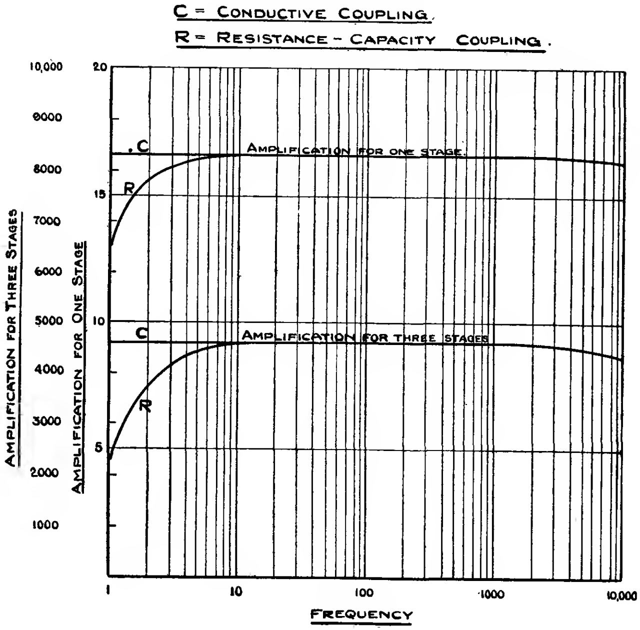

Fig. 5. Amplifier characteristics.

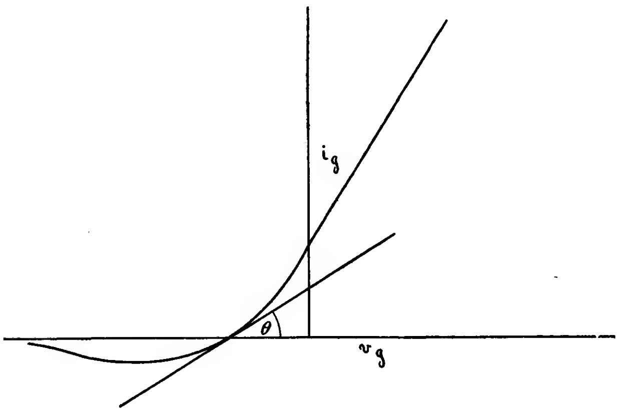

Fig. 6.

factor was 0·01, so we can neglect the term R_c. G_l is the conductivity of the leak in the case when grid bias is used and when a free grid system is adopted Y' is increased by G_g where G_g is given by the backlash of the grid current curve. In Fig. 6 the grid will take up a potential where the grid current is zero and then

$\cot\theta = \frac{v_g}{i_g} = R_g$. For an actual measured case R_g was found to be $80 . 10^6$ and so we get $G_g = 1{\cdot}25 . 10^{-8}$. Using these values we obtain the characteristics shown in Fig. 7. With a leak of 2 megohms we obtain a characteristic which maintains e/i constant from zero frequency up to 100 cycles per second. Above this frequency there is a rapid drop in the ratio and at 10,000 cycles the ratio is only 4·3 per cent. of what it is at zero. As the value of the leak is increased the sensitivity is increased proportionately at low frequencies but the cut-off begins at lower frequencies. With no leak, the grid filament conductivity G_g acts as an effective upper leak limit (80 megohms in this case).

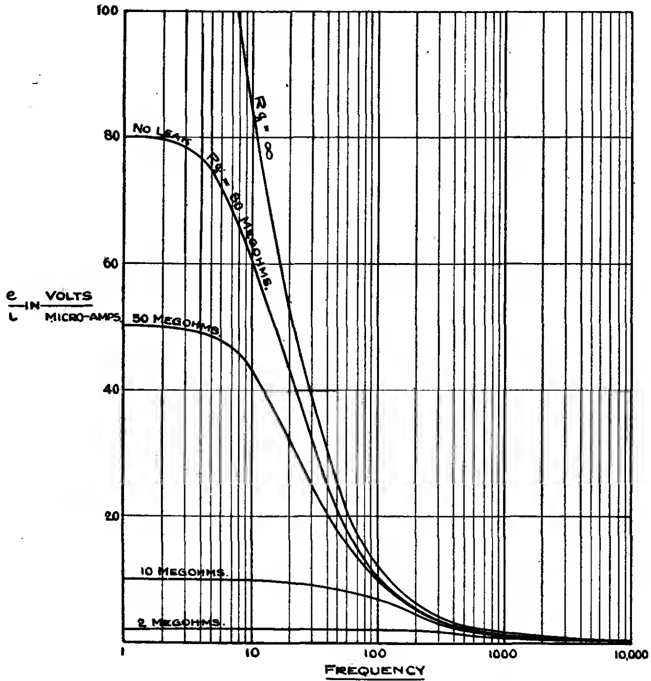

Fig. 7. Photo-electric cell characteristics.

The overall current sensitivity

By combining the characteristics of the cell with those of the amplifier and power valve we can obtain the overall current sensitivity. This is plotted in Fig. 8. Curves C refer to conductive coupling and curves R to resistance capacity coupling. It will be seen that the current sensitivity is of the order of 10^8 and is dependent upon the frequency, having a maximum value for some frequency determined by the characteristics of the amplifier. If conductive coupling is used, no low-frequency cut-off is obtained and then the greatest current sensitivity occurs at the lowest possible frequencies.

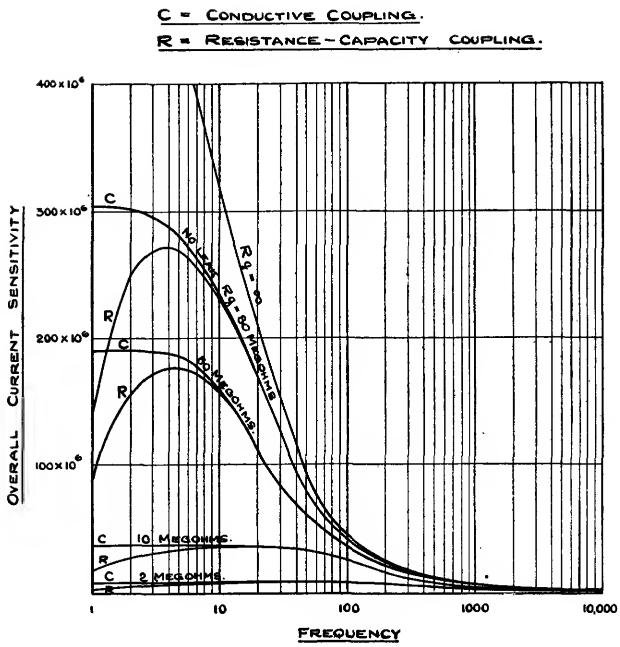

Fig. 8. Overall characteristics.

§ 7. CONCLUSIONS

(1) The current sensitivity of a photo-electric cell and amplifier is affected by the input impedance of the amplifier.

(2) This impedance is so important in all practical cases that the sensitivity is materially reduced as the frequency is raised.

(3) With conductive coupling the maximum sensitivity is obtained at very low frequencies of the order of 1 or 2 per second.

(4) With resistance capacity coupling, the maximum sensitivity is obtained at some frequency greater than zero. This frequency rises as the value of the leak resistance is reduced.

(5) A very high leak resistance or a free grid connexion gives the greatest sensitivity at very low frequencies, but when the frequency rises to the order of 500 per second there is no merit in having such a high leak resistance.

(6) With this very high leak resistance or free grid connexion, the sensitivity rapidly falls with increasing frequency.

(7) The use of a low leak reduces the sensitivity proportionately but gives a superior response characteristic over the frequency range. We can obtain the relative sensitivity by taking the grid filament resistance as the highest possible leak and multiplying the sensitivity with this leak by the ratio of the actual leak to the grid filament resistance with free grid connexion. To obtain anything approaching a uniform response characteristic it is necessary that the sensitivity be reduced to about 0·25 per cent. of the maximum.

(8). The highest sensitivity will be obtained at very low frequencies by using a valve having a high voltage factor and a small grid current backlash, i.e. with R_g very large. In this case low-capacity leads are not of great importance, since the input capacity of the amplifier is large.

(9) To obtain a uniform response characteristic, we desire to reduce Y' and Y_c. Y' can be reduced by using a low-factor low-impedance valve with a low-anode circuit resistance, but Y_c' cannot be reduced below the value of the cell. In this case low-capacity leads are necessary, since the input capacity of the amplifier is small.

DISTORTION IN THE AMPLIFICATION OF PHOTO-ELECTRIC CURRENTS AND A REMEDY

By Dr HEINRICH GEFFCKEN and Dr HANS RICHTER,
Laboratories of Mr Otto Pressler, Leipzig.

MS. received May 6, 1930. *Read June* 5, 1930.

ABSTRACT. The effect of distortion in the amplification of photo-electric currents is dealt with, and a new type of cell is described which gives very much higher sensitivity under certain voltage conditions. The cause of the particular phenomenon which conduces to this result is discussed.

§ 1. AMPLIFICATION OF PHOTO-ELECTRIC CURRENTS

ONE of the main advantages which is always emphasised, when comparing photo-electric cells with other light-sensitive cells, is the absolute proportionality which exists between photo-electric current and illumination. This is of particular importance in connexion with measurements and for the speaking film. It is, however, but seldom mentioned that this accurate proportionality is lost whenever the currents are amplified when using gas-filled cells. The reason is as follows.

The sensitivity of the gas-filled cell increases rapidly, as is well known, with the applied voltage. For the purpose of amplifying a photo-electric current, it is usual, as shown in Fig. 1, to place the cell 1 in series with a resistance 2 and to transfer the voltage variations at the point 3 directly, or by means of a condenser to the grid of the triode 4. With this arrangement any increase in illumination, and therefore in the

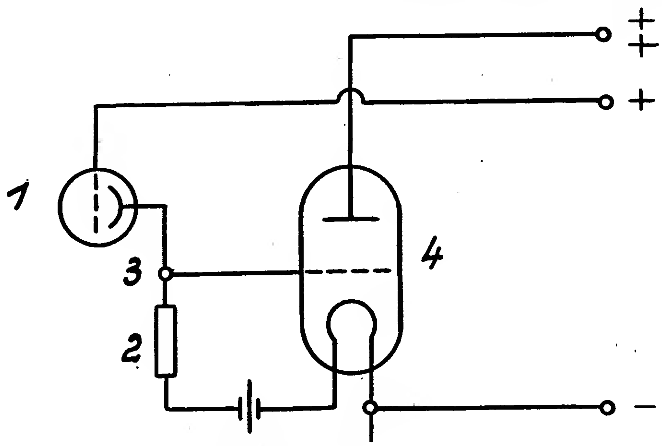

Fig. 1. Usual circuit for amplification of photo-electric currents.

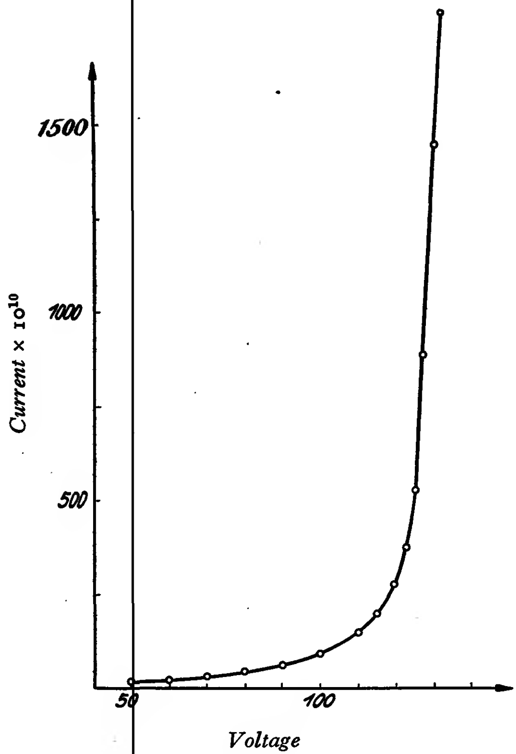

Fig. 2. Relation between sensitivity and voltage.

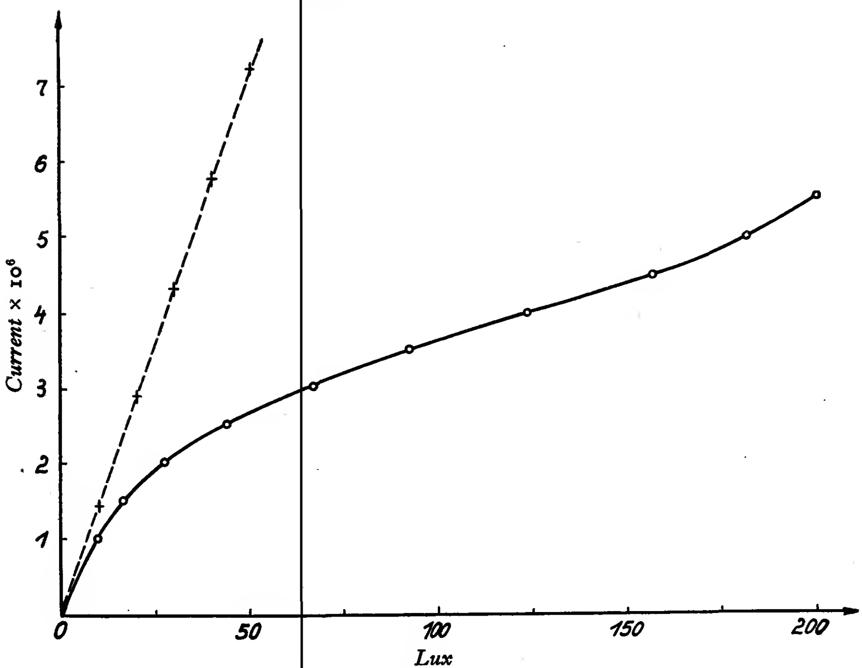

Fig. 3. Relation between current and illumination.

photo-electric current in the cell 1, also increases the potential drop at the resistance 2, thereby reducing the voltage applied to the cell and consequently its sensitivity. If, for example, we double the illumination, we obtain by no means twice the photo-electric current, because this increased illumination reduces at the same time the sensitivity of the cell. It is obvious that the curve representing the relation between illumination and photo-electric current in such an amplifying circuit must depart from a straight line and curve downwards according to a function which can be ascertained by calculation, graphically, or empirically from the graph representing the relation between voltage and sensitivity of each particular cell and from the amount of the resistance 2.

Fig. 2 shows, for our experimental cell, the relation between voltage and photo-electric current, and Fig. 3, for the same cell, the relation between illumination and photo-electric current, assuming a total voltage of 130 and a series resistance of 2 megohms. Measurement by means of a reflecting galvanometer in a practically resistance-free circuit gives the broken straight line which is shown in Fig. 3. It is quite clear that the use of such a circuit for measuring purposes results in falsification of the results and, in the case of a speaking film, a weakening of the high amplitudes and consequently the appearance of disturbing upper harmonics.

§ 2. DESCRIPTION OF NEW CELL

We set ourselves the task of eliminating this defect by constructing a photo-electric cell the sensitivity of which is less dependent upon variations in the voltage than present types. The obvious way to accomplish this aim was the use of an auxiliary anode at a constant potential, in a manner similar to the screened grid in the valve, which should reduce the influence of the main anode upon the discharge within the cell. This method proved very suitable, though in a different sense from what we originally expected. Figs. 4 and 5 show a cell designed by us on these lines. Opposite the cathode 5 are arranged two grid or net-shaped anodes 6 and 7, and a definite potential is established between the cathode 5 and the auxiliary anode 6; assuming the cathode potential as zero point, we can vary the voltage between the anode 7 and the cathode 5 whilst keeping the illumination of the cell constant, and Fig. 6 shows graphically the relation between the photo-electric current thus measured between the cathode 5 and the auxiliary anode 6 for the voltage of 100. Although there is no trace of screened effect this is quite explicable: the phenomena in gas-filled photo-electric cells cannot be compared with those in the vacuum tube, but resemble the conditions in the glow tube. The only factor of importance is the field produced by space charges immediately near the light-sensitive film, whilst regions away from the film are only of interest in connexion with special problems such as inertia.

§ 3. CHARACTERISTICS OF CELL

A remarkable condition is noticed when the potential of the auxiliary anode 6 is still further increased so that it approaches the discharge potential. This is shown in Fig. 7, which refers to the same cell as was used for obtaining Fig. 6, but with an auxiliary anode voltage of 125. The characteristic is, generally speaking, of normal shape, but between 130 and 140 volts there is a range in which it runs practically

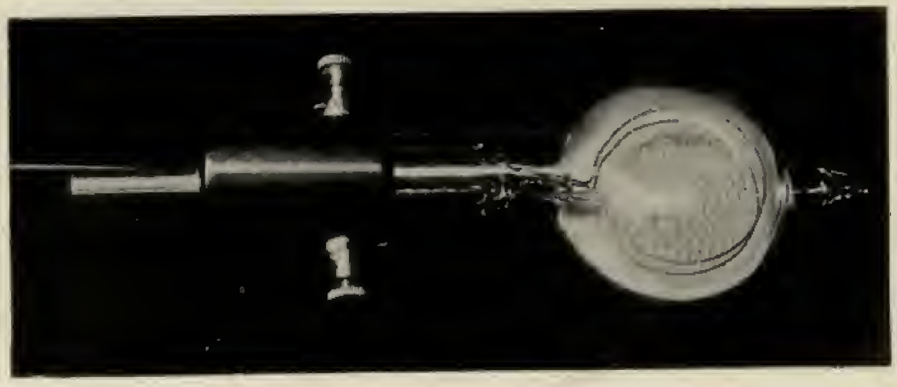

Fig. 4. New screened cell.

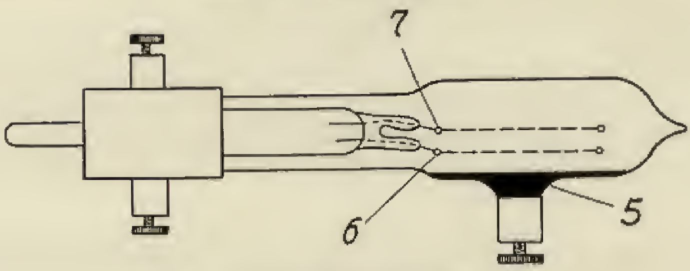

Fig. 5. Diagram of new screened cell.

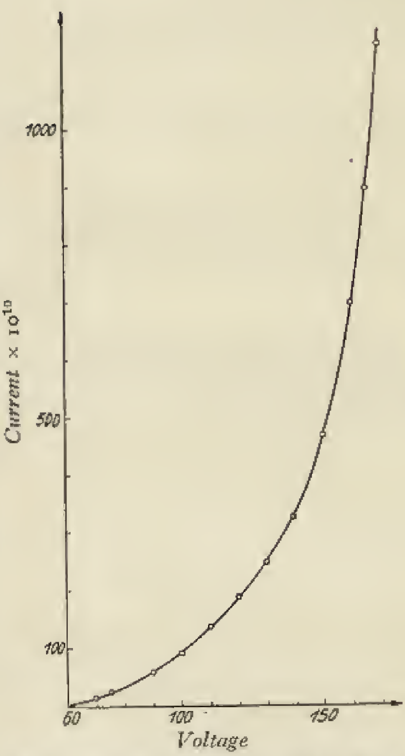

Fig. 6. Characteristic of new cell for voltage of 100 between cathode and auxiliary anode.

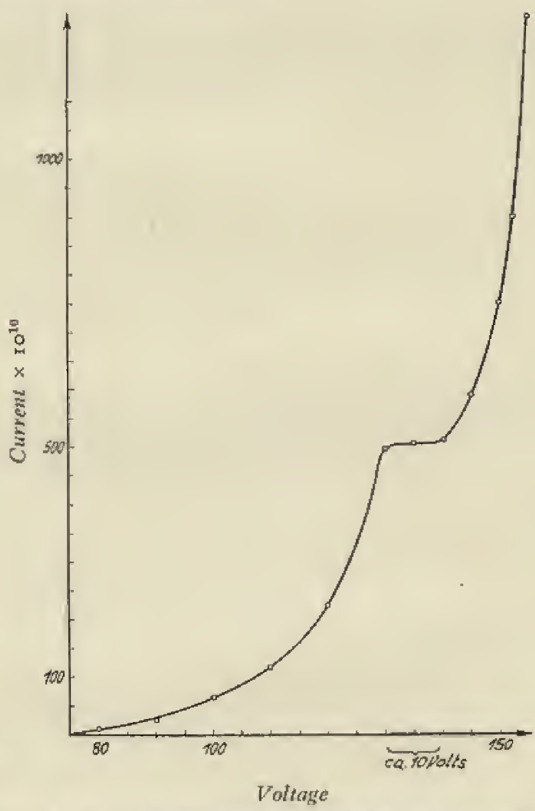

Fig. 7. Characteristic of new cell for voltage of 125 between cathode and auxiliary anode.

horizontal, and for a sufficient width to enable full control of the triode valve. Within this zone the cell functions like a vacuum cell with, of course, a very much higher sensitivity. The critical potential for the auxiliary anode, for which this remarkable effect—so extremely important for amplification—arises, is pretty sharply defined. A reduction of only 5 volts in this potential changes the curve so that the flat portion inclines about 20 degrees to the horizontal, whilst a similar increase of potential produces a decline of the curve to the horizontal. The characteristic therefore shows two points of reversal, which at first sight correspond to that of the dynatron. In this condition the cell represents a "negative resistance" so that it can be used for generating oscillations or trigger effects for relay purposes. The oscillations enable the inertia of the effect to be studied, but this is too small to be of any effect in speaking films. Our corresponding measurements have not yet been completed.

The explanation of this remarkable phenomenon might be found in the fact that, when the potential of the auxiliary anode is sufficiently high, all ionisation takes place in the space between the cathode 5 and the anode 6, but when the potential of the main anode 7 increases to the same level as that of the anode 6 ionisation is transferred more and more to the space between the anodes 6 and 7. The electrons emanating from the cathode 5 push forward from the space 5–6 through the auxiliary anode, then into the space 6–7 and produce ionisation there. As a consequence of this shifting of the ionisation space, a large number of the gas ions are transferred into a field of very low potential gradient and the probability of recombinations is increased. Besides, many of the ions are neutralised by the auxiliary anode so that a lesser number of ions reaches the cathode 5 and reduces the electron emission on the cathode due to ionic bombardment. The above explanation is confirmed by the experiment, because on passing through the above voltage range one can notice a change of the auxiliary anode current from positive to negative.

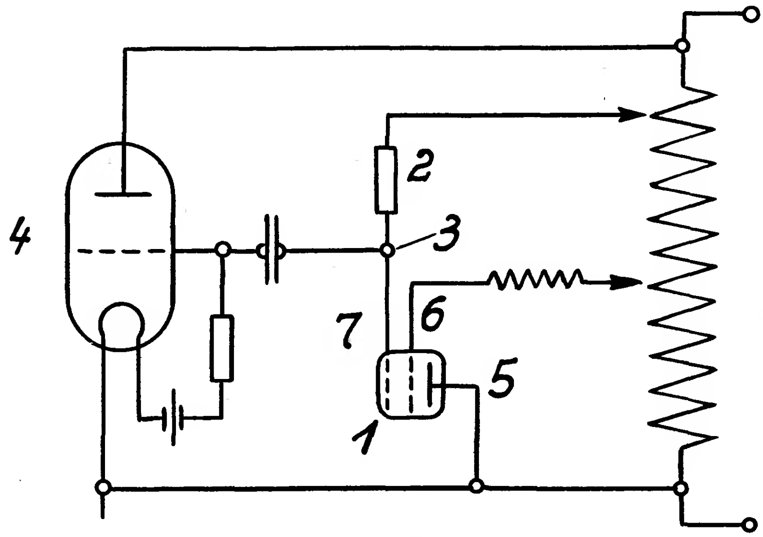

Fig. 8. Circuit for new cell.

§ 4. METHOD OF CONNECTING CELL

Fig. 8 shows the way in which the new cell is connected to the first amplifying tube; for the sake of clearness only a normal grid tube has been shown. The cell 1 is on the negative side and the series resistance 2 on the positive side; the auxiliary anode 6 is at constant potential. The positive potential of the series resistance 2 is so adjusted that for a given average illumination the voltage between the main anode 7 and the cathode 5 should be within the flat range of the characteristic (Fig. 7). The transfer of the voltage variations at the point 3 to the grid of the valve 4 takes place by means of capacity as usual.

The reproduction of sound with this new cell is remarkably pure and practically free from the well-known disturbing harmonics.

A METHOD OF MEASURING SMALL ANGLES

By D. S. PERFECT, M.A., D.Phil., F.Inst.P.,

Optics Department, The National Physical Laboratory.

MS. received May 3, 1930. *Read June* 5, 1930.

ABSTRACT. The paper describes a method of measuring angles less than 15 seconds with a probable error of the order of 0·05 sec. Settings are made by causing an image of a fine slit to fall on the edge of a steel prism worked to razor-like sharpness. The prism divides the beam of light into two components, the relative intensity of which forms the criterion of the position of the image of the slit. The relative intensity is measured by allowing the component beams to fall in rapid succession on a photo-electric cell, the ripple in the current through which, due to any inequality of the intensities, is amplified by a low-frequency amplifier. The alternating current from the amplifier is rectified by a commutator, and the rectified current, measured by a galvanometer, is taken as a measure of the relative intensity of the two components. Displacements of the beam of light which forms the image of the slit are measured by giving a compensatory displacement by means of a hollow prism, the internal air-pressure of which is varied and measured.

§ 1. INTRODUCTION

THE accuracy of visual methods of making the optical settings upon which the measurement of angles depends varies greatly with the skill of the observer, and is finally limited by the properties of his eyes and by his powers of judgment. In the method described in the present paper the criterion of setting may be said to be purely physical in as far as personal judgment is only required in reading the scale of a galvanometer, and is not the factor which limits sensitivity.

§ 2. GENERAL DESCRIPTION

The apparatus is shown diagrammatically in Fig. 1. By means of the lens L_3 and the prism P_3 an image of the filament of the lamp λ is focussed on the narrow slit S. The light proceeding from this slit, after collimation by the telescope objective L, passes through the hollow prism Π, and is reflected by the plane mirror M. M is set approximately normal to the incident beam, but with a slight tilt, so that the reflected beam traverses an adjacent path, and an image of the slit S is formed on the edge of a 90° prism p, placed immediately below S.

The prism p is made of stainless steel, and is polished so that the two faces meet in an edge of razor-like sharpness. The light incident on the edge of p is cleanly divided into two components, the relative energies in which depend acutely on the relative position of the image and the edge of the prism, that is, on the orientation of the mirror M. If, then, it is possible accurately to determine a given relative intensity of the components (in practice their equality) there is available an accurate criterion of a particular direction of the return beam of light incident on the lens L.

Any small rotation given to the mirror M can be measured by adjusting the refractive index of the prism Π until the beam of light returns to the lens L in its original direction, as determined by the above criterion. The micrometer formed by the hollow prism Π has been previously described*. The refractive index is varied by changing the internal air-pressure, which is read on a mercury barometer. A change of barometric height of approximately 5 cm. produces a deviation of 1 sec. of arc in the light traversing the prism (the sensitivity is calculable very accurately from a rough measurement of the angle of the prism and from the known properties of air), so that if the barometer is read to 1 mm. the uncertainty in angle will not exceed 0·02 sec.

The optical system described above and shown in Fig. 1 is the simplest to which the method may be applied, and by converting angular into linear movement has applications to the comparison of lengths. A further application of the method is the goniometry of prisms. For this purpose the optical system may be modified by replacing the mirror M by the prism P (Fig. 2) and successively by the two mirrors M_1, M_2. The method of simple substitution is then used†.

To return to the criterion of direction, the detecting system used to determine the equality of the two components is essentially that described elsewhere in this Discussion‡. It was not until the development of this detector that the present scheme was tried out. It would of course have been possible to employ the method of balancing two cells§, but previous experience with that method indicated that the secular changes which are inseparable from its use would have been fatal to the accuracy required for the angle measurements. The two components reflected from the prism p (Fig. 1) are made parallel by the 45° prisms P_1, P_2 and collimated by the lenses L_1, L_2. They then pass through circular apertures about 4 mm. in diameter in the templet plate t, by means of which their cross-sections are accurately defined. After successive interruption by the sector disc d, they are directed by the 45° prisms P_4, P_5 on to the photo-electric cell C. The concave lens L_4 is placed so that the cell is irradiated over most of the sensitive area. The prisms P_4, P_5 are relatively adjusted so that the same area of the cell is illuminated by both components. Any departure from equality in the intensities of the two components produces a ripple in the photo-electric current which is amplified by the amplifier A. The resulting alternating current is rectified by the commutator k (attached to the shaft of d) and indicated on the scale of the galvanometer G. The deflection of the galvanometer is then reduced to zero by suitably adjusting the refractive index of the prism Π.

* D. S. Perfect, "An application of the interferometer to the goniometry of prisms," *Trans. Opt. Soc.* **30**, 118 (1928–9).

† J. Guild, "Angle comparators of high precision for the goniometry of prisms," *Trans. Opt. Soc.* **23**, 297 (1921–2); D. S. Perfect, *loc. cit.*

‡ G. M. B. Dobson and D. S. Perfect, "A method of comparing very small amounts of light by means of a photo-electric cell and a valve amplifier," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 79 (1930); see also D. S. Perfect, "Spectrophotometric absorption measurements," *ibid.* p. 182.

§ D. S. Perfect, "Spectrophotometric absorption measurements," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 180 (1930).

§ 3. DETAILS OF CONSTRUCTION

For the sake of rigidity the entire system was mounted on a cast iron table T (6×3 ft.). The lamp λ and lens L_3 were mounted as a unit on three legs of which one was adjustable in height. The parts $P_1, P_2, P_3, L_1, L_2, S$ were all mounted on a single base whose three legs rested on the table. The width of the slit S was 0·16 mm. The lens L, of focal length 125 cm., was mounted on a **V**-support with its tilt adjustable, and the prism Π was mounted on a steel gauge of suitable height. M was mounted on a table with three levelling screws which rested in **V**-grooves on a second and rotatable table. A steel ball fastened to the underside of this table rested between three steel balls fastened to a bar clamped to the table. This arrangement defined the centre of rotation and the remaining constraints were imposed by the steel balls x, y fastened to a cross bar. Adjustment could be given to the orientation of the table by means of the screw a.

The apparatus for fine adjustment of the beam of light by means of the micrometer Π was similar to that described in the paper already cited*.

§ 4. CONCLUSION

By means of this equipment it is possible to measure small angles (not exceeding about 15 seconds) with a probable error of less than 0·05 sec. The accuracy is limited not by the available sensitivity, which is enormous, but (as in the other work in which this detector is used†) by the unsteadiness of the detecting system. Any improvement of the system subsequently achieved will immediately reduce the probable error, whereas only the evolution of a super-man can improve the visual accuracy. It is probable that, were the unsteadiness of the detector removed, the increased accuracy would reveal the presence of residual effects due to temperature changes and lack of rigidity in the optical system, and demand the introduction of further precautions which it has hitherto been needless to take. It is possible to obtain greater effective sensitivity by increasing the energy density at the central region of the image formed on the dividing prism p. This may be achieved by increasing the intrinsic brightness of the source or by increasing the aperture of the system. It is advantageous in any event to make the aperture as large as is convenient, because the larger the aperture the narrower the slit S can be made without diminishing the central energy density; and an unduly wide slit, by adding to the total energy of each component beam, causes a decrease in the sensitivity.

* D. S. Perfect, *Trans. Opt. Soc.* **30**, 118 (1928–9).

† See Dobson and Perfect, and Perfect, *loc. cit.*

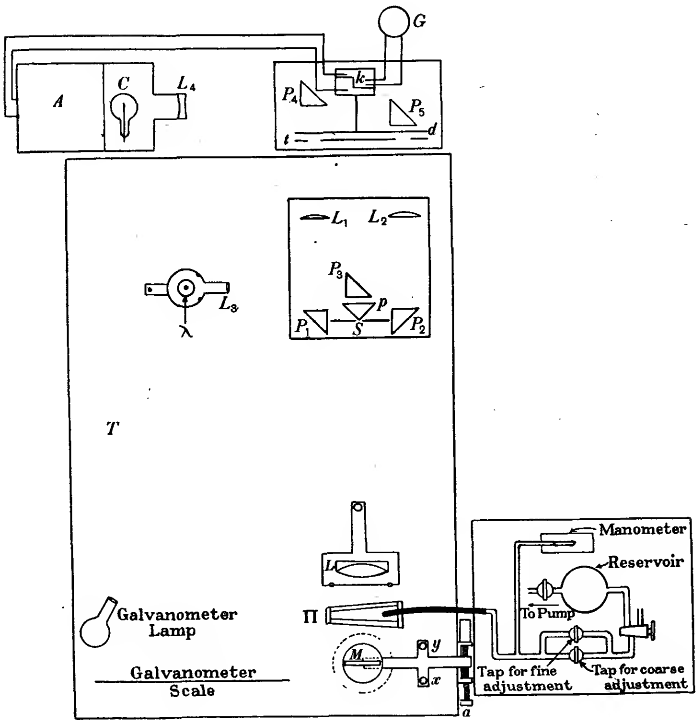
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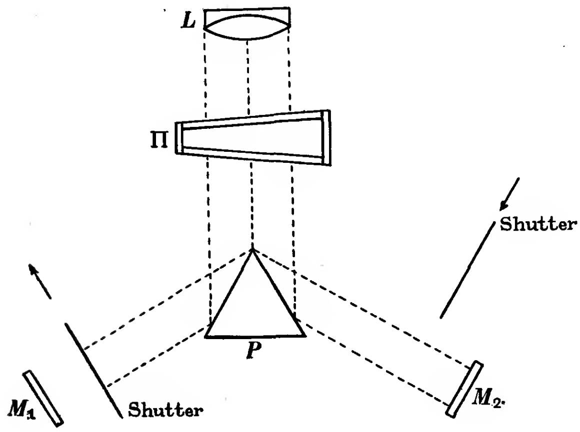
Fig. 1.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M_2

Fig. 2.

NOTES ON PHOTO-ELECTRIC PHOTOMETRY

By CLAYTON H. SHARP, Ph.D.,
Technical Adviser, Electrical Testing Laboratories, New York.

MS. received April 29, 1930. *Read June* 5, 1930.

ABSTRACT. An attempt is made to classify and describe briefly certain methods of photo-electric photometry which have come under the writer's observation and have proved their practical utility through extensive use in commercial laboratories over a period of some years. The methods of procedure are divided into three classes: Class 1, involving linearity of valve response and amount of amplification; Class 2, involving linearity of cell response alone; Class 3, involving linearity of neither cell nor amplifier. Problems connected with the measurement of the transmission of colour filters, work in the ultra-violet, colour response, and colour matching are discussed. The conclusion is reached that photo-electric methods of photometry are much superior to the older methods, at least in connexion with the production and testing of incandescent lamps on a large scale.

§ 1. INTRODUCTION

Of all the applications of the photo-electric cell perhaps its use in photometry exacts more of it than any other. While in other applications approximate linearity of response and approximate constancy of sensitivity are sufficient and the question of colour response is, in general, of no great importance, in photometry some or all of these requirements are much more rigid, so that deviations from the ideal condition, which in other cases might be of no practical significance, here become major factors.

Recognising the many excellent papers which have been written on this subject, a citation of which is unnecessary for the present purpose, and, in particular, the admirable treatment, especially from a theoretical point of view, in the recent book on photo-electric cells by Campbell and Ritchie, it is the purpose of this paper to classify and to describe in not too detailed a manner certain methods which have come under the writer's observation and have proved their practical utility through extensive use in commercial laboratories over a period of some years.

In its simplest form a photo-electric photometer involves a photo-electric cell, a battery, and a galvanometer or electrometer which measures the current produced under the influence of the illumination on the cell and, hence, gives a reading proportional to that illumination. This simple method of application, useful as it is in a great deal of laboratory work, is not well adapted to photometry on a more industrial scale, largely because of the practical difficulties of the rapid and certain measurement of small electric currents. For this reason the obvious step has been taken of introducing amplification by means of valves, thereby enabling better methods and less delicate apparatus to be employed.

§2. CLASSIFICATION OF METHODS OF PROCEDURE

As soon as the principle of amplification is adapted there is abundant opportunity for devising different types of connexion and systems of measurement, and a considerable variety of these has been proposed. Three general classes of procedure may be distinguished in this regard: Class 1, where the photometric measurements are made in terms of variations in the plate-circuit of a valve, thus involving directly the linearity of the valve response and the amount of amplification introduced; Class 2, where the linearity and amplification of the valve do not enter directly into the result but only the linearity of the cell response is involved; Class 3, where the linearity of neither cell nor amplifier is required.

Class 1, involving linearity of valve response and amount of amplification

An example of Class 1 is the photometric arrangement developed and used by the Westinghouse Lamp Company in Bloomfield, N.J. The diagram of Fig. 1 shows the circuit employed*. The cathode of the photo-electric cell is connected directly

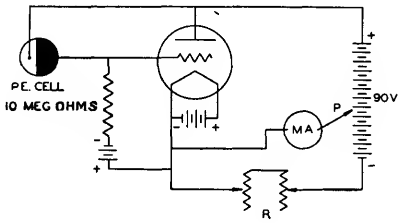

Fig. 1. Westinghouse Lamp Co.'s circuit.

to the grid of an amplifier tube. Between the grid and the filament a high resistance is connected. Between the negative terminal of the anode battery and the filament is an adjustable resistance R. A milliammeter is connected between the filament and a suitable point P on the anode battery, so that with the cell in the dark a suitable adjustment of R will produce the condition that the milliammeter indicates zero. Next, the photo-electric cell is exposed to the illumination of a standard lamp of known value and, by adjusting either the distance between the cell and the source or an iris diaphragm placed in front of the photo-electric cell, the milliammeter is brought to a reading which corresponds to the assigned value of the standard lamp. Thereafter, the readings of the milliammeter are directly interpretable in terms of the output of the lamps being measured.

It will be seen that the results vary in accordance with the characteristics of the photo-electric cell, of the amplifier, and of the voltages applied thereto. A disadvantage of this arrangement is that the voltage on the photo-electric cell, when the cell is delivering current, is less than the voltage on the cell when dark by an amount equal to the voltage drop of the photo-electric current in the high resistance connected between the grid and filament. Unless a vacuum type of photo-electric cell is used and the applied voltage is well above the saturation voltage of the cell,

* St John, *Trans. Ill. Eng. Soc.* **23**, 441 (1928).

a departure from linearity of response may readily occur. In fact, in using this arrangement it has been found necessary to adapt the photo-electric cell to the rest of the circuit in order that linearity may be attained. With respect to convenience and speed this arrangement leaves little to be desired.

Class 2, involving linearity of cell response alone

As an example of Class 2 photometers, that is, where linearity of the response of the cell is required but the characteristics of the valve are eliminated as direct factors, the apparatus which is shown diagrammatically in Fig. 2 and has been developed and used at the Electrical Testing Laboratories may serve*. With this arrangement an amplifier bridge is used with the cathode of the cell connected to the

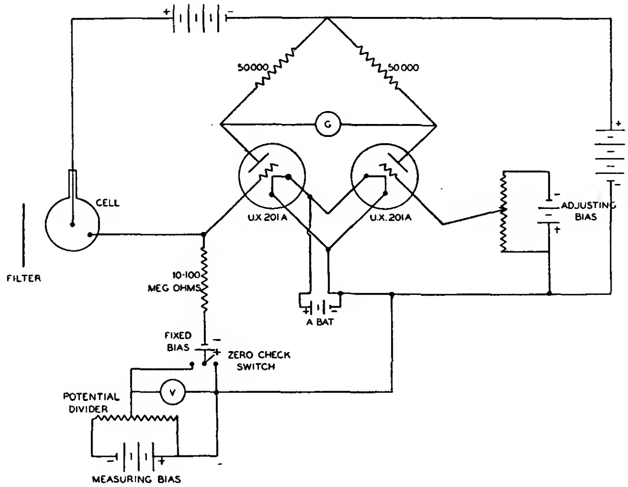

Fig. 2. Photo-electric cell with amplifier bridge and measuring bias.

grid of one valve. The high resistance connected to this portion of the circuit goes to a potential divider whereby the degree of voltage bias on the grid may be adjusted. A similar divider is provided for the grid of the other tube. To operate, the variable bias on the first tube is made zero with the cell dark and the bias of the second tube is adjusted to the point where the bridge is balanced. Then, when the cell is exposed to light, the bridge is thrown out of balance and the balance is once more restored by applying an additional biasing voltage to the grid of the first tube. The amount of the voltage so applied is a measure of a photo-electric current and hence of the intensity of the light falling on the cell. This voltage may be read either by a suitable voltmeter or simply from graduation on the potential divider. It is evidently simple to introduce adjusting resistances so that these readings come out directly in candle-power or lumens as required.

This procedure has the ordinary advantages of a zero or null method. The voltage on the photo-electric cell is undisturbed, the amount of amplification and

* Sharp and Smith, *Trans. Ill. Eng. Soc.* **23**, 434 (1928).

the linearity of the grid voltage-plate current relationship of the valves do not enter in, and at the same time any small variations of filament voltage have little effect on the dark balance. The vital points are that the cell should have a linear response and that the grid resistor should be stable and constant. The rest of the apparatus serves simply as an amplifier voltmeter to read the fall of potential on the grid resistor.

Class 3, *involving linearity of neither cell nor amplifier*

In Class 3 photometers the photo-electric cell serves simply to balance the illumination produced by the test lamp against the known illumination produced by a comparison lamp. The apparatus shown in Fig. 3*, also a product of the Electrical Testing Laboratories, may be cited. In this arrangement the test lamp,

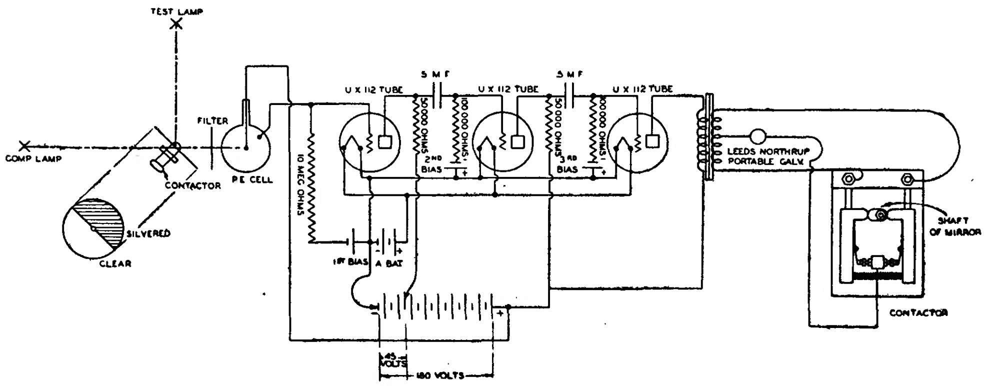

Fig. 3. Photo-electric photometer using rotating mirror and amplifiers.

which is usually in an integrating sphere, and the comparison lamp, which travels on a track with a scale graduated in photometric quantities, shine alternately on the photo-electric cell. To produce this condition of alternation a glass disc which is silvered on one half is placed as shown in the diagram, and the light from the comparison lamp shines on the cell when the clear portion of the disc is in its path, while the test lamp shines on the cell when the silvered half comes in line. The disc is rotated by a motor and drives with its shaft a contactor, the use of which will be referred to later.

The cell is connected to an amplifying train of conventional make-up and in the anode circuit of the last tube is introduced the primary of a transformer. The secondary of the transformer is tapped at the mid-point and the tap leads through a rugged galvanometer to the mid-point of the contactor. The terminals of the secondary winding lead to the other contacts and the contactor is driven by a cam on the shaft of the rotating element as stated. The whole arrangement is so timed that one contact is closed during the transit from test lamp to comparison lamp and the other contact during the transit from comparison lamp to test lamp, the switching being done in the intermediate periods while the light on the cell is constant, and

* Sharp and Kinsley, *Trans. Ill. Eng. Soc.* **21**, 125 (1926); Sharp and Smith, *ibid.* **23**, 429 (1928).

hence there is no current in the secondary circuit of the transformer. With this circuit, if the illumination on the cell produced by the test lamp is higher than that produced by the comparison lamp, the galvanometer deflects in one direction, and vice versa. When the two are balanced the galvanometer remains at zero. The condition of balance is produced by moving the comparison lamp, and the corresponding photometric value is read from the scale connected therewith. It will be seen that the linearity of the amplifying train or of the photo-electric cell does not come into the question. The cell serves the same purpose as the eye in the ordinary photometer and indicates merely when the condition of equality between two illuminated surfaces has been attained.

§ 3. GENERAL CONSIDERATIONS

In the case of all the above appliances the photo-electric cell with its modifying train is placed in a heavy box of copper or aluminium for the purpose of cutting out electric and magnetic disturbances. When used in connexion with an integrating sphere the aperture in the sphere through which the light emerges is covered with diffusing glass which forms a portion of the inner surface of the sphere. Where a comparison lamp moving on a track is employed its light falls on a diffusing glass placed in front of the photo-electric cell, thus obviating the possibility of errors due to lack of conformity with the inverse square law.

For ordinary photometry the experience of the Electrical Testing Laboratories has shown that of the three types considered, Class 3, namely, the rotating mirror apparatus, is on the whole somewhat more reliable and satisfactory than Class 2. Five integrating spheres are continuously at work with photo-electric photometers of these two types, and optical photometry in the ordinary testing of incandescent lamps has been abandoned with a resultant notable increase in accuracy of the work and decrease of cost.

The measuring bias apparatus is used with great advantage in connexion with the measurement of the distribution of candle-power about lamps with reflectors or globes. In doing this sort of work the entire lamp with its reflector is rotated at a relatively slow speed so that the measurement at any given vertical angle may represent an average intensity for the corresponding zone. The slow speed is required in order not to disturb the gas currents, and hence the intensity of the lamp. It results, however, in many cases, in a very strong flicker of the light and this flicker in the case of optical photometry makes accurate settings practically impossible. With the photo-electric photometer the flicker is shown by corresponding excursions of the galvanometer spot to one side and the other and the true zero reading can be estimated with satisfactory accuracy.

§ 4. TRANSMISSION OF COLOUR FILTERS

The same type of apparatus is used in getting transmission values of colour filters. In this work a broad filament is focused on the slip of a spectrometer and the photo-electric cell is placed to receive the emergent light, the eyepiece having been removed. Any one of three procedures can be used in making such measurements.

1. The amplifying bridge is balanced with the cell dark and galvanometer deflections are read with the full light and with the filtered light.

2. The measuring bias is adjusted to reduce the readings to zero successively with the full light and the filtered light.

3. A Brodhun adjustable sector is put in the entering beam. The filter is interposed, the sector is opened to the division marked 100, and the reading of the galvanometer is noted. Then the filter is removed and the sector is closed to the point where the galvanometer gives the same reading. The reading on the sector then gives the percentage transmission. The last procedure is found to be the most convenient within the visible spectrum.

§ 5. WORK IN THE ULTRA-VIOLET

In corresponding work in the ultra-violet the variable sector cannot be used because of its glass parts nor can the ordinary photo-electric cell be employed. With a sodium-in-quartz cell and with a quartz monochromator the transmission of various media in the ultra-violet can be measured with no other difficulties than those which arise from the unsteadiness of the light source, and the sensitivity is much higher than is obtainable by the use of a thermopile. The response curve of the same arrangement can be measured by setting the apparatus so that a thermopile can be slipped in between the photo-electric cell and the tube of the monochromator and taking successive readings. The apparatus then becomes adaptable to the determination of energy curves in the ultra-violet. In this case, however, the conditions have to be carefully controlled to see that no change in sensitivity occurs.

A procedure for the measurement of ultra-violet lamps, in terms roughly of their erythema-producing effect, has been worked out, being based on work done by Dorcas and Forbes* who have shown that by the combination of a cell containing a solution of picric acid with a red-purple corex glass transmitting ultra-violet, and a clear corex glass cutting off the ultra-violet beyond 2700 Å, a transmission curve approximating the erythema curve of Hausser and Vahle is obtained. With the sodium photo-electric cell the approximation to the erythema effect obtained with such a filter is better than with a thermopile. A combination of this sort seems to offer one of the best means at present available for the comparison of ultra-violet sources of a given type with each other in terms of erythema effect.

§ 6. COLOUR RESPONSE

An outstanding question which is vital in the use of the photo-electric cell in photometry is that of colour response. The basis of ordinary photometry is the adjustment of two fields to equality of brightness as judged by the human eye. If the colour of the two fields is the same it makes no great difference what eye judges them. If, however, they differ in colour the judgment will be affected. The standard eye is the one described through the visibility factors adopted by the International Commission on Illumination. A similar state of affairs applies to the photo-electric cell except that photo-electric cells do not respond to the different spectral regions like any human eye whatever. A thin layer caesium cell seems to come closest to

* Dorcas and Forbes, *Journ. Amer. Chem. Soc.* **49**, 3081 (1927).

giving the eye response, but as a practical matter any photo-electric cell requires correction usually by the interposition of coloured filters in order that it may compare lights of different colours with an acceptable degree of accuracy. Some of the caesium cells require a light amber filter and others require a light blue filter. There is no high degree of uniformity in the commercial product and a suitable filter must be selected for each cell. An unfortunate part of it is that many cells apparently shift their colour response from time to time, requiring a readjustment of the filter.

In this connexion, it is important to note that Campbell and Ritchie have indicated the feasibility of using two photo-electric cells, one blue-sensitive and the other red-sensitive, and attaining a colour compensation by adjusting the relative responses of the two cells.

As a practical matter the accuracy of the adjustment for colour correction can be determined by measuring a series of standard lamps ranging from, say, the 25-watt vacuum lamp, which is relatively reddish in colour, to the 200-watt gas-filled lamp which is far whiter. If these lamps give their standard values consistently the photometer is evidently reading in a manner concordant with the eye with which these standards were made. Usually a photometer is used in connexion with an integrating sphere and in this case the sphere paint, if not absolutely white, intervenes to modify the colour of the light issuing from the sphere. Therefore the filter required by a given photo-electric cell may not be quite the same when the cell is used with the integrating sphere as when the cell receives the unmodified light of the lamp. Sometimes it is convenient to use a wedge-shaped filter so that it can be inserted to a greater or less distance in front of the window of the sphere.

§ 7. COLOUR MATCHING

A matter allied to photometry in which photo-electric methods are applicable with advantageous results is that of colour matching, particularly the matching of the colours of incandescent lamps with each other and hence determining their equality in colour temperature. Dr Campbell of the General Electric Company's Research Laboratory at Wembley was the pioneer in this field and developed methods of great sensitivity which have been described in scientific publications and also in the work by Campbell and Ritchie. Winch* has modified Campbell's methods, notably in the use of an amplifying circuit similar to that described under Class 2 above.

The rotating mirror photometer scheme has been adapted† to colour matching by substituting for the rotating mirror a rotating disc, one-half of which is red and the other blue (see Fig. 4). The apparatus is placed so that the light from the lamp to be measured passes directly through this disc to the photo-electric cell. Evidently, when the disc is rotated the cell receives in alternation red-filtered and blue-filtered components of the light of the lamp and with a proper combination of cell and filters the corresponding currents will balance each other at some one value of the colour temperature of the lamp filament. If a yellowish filter is interposed, the apparent

* Winch, *Journ. Scient. Instr.* **6**, 374 (1929).

† Sharp, *Journ. Opt. Soc. Amer.* **20**, 62 (1930).

colour temperature of the lamp becomes lower and it is necessary to raise its temperature in order that the balancing point can be found. It follows that by the use of a combination of fixed filters, either blue or amber, and a corresponding tapering or wedge filter a balancing point can be obtained for any desired colour temperature. After such a balance has been obtained the corresponding colour temperature can be determined by substituting a standardised lamp and finding the voltage at which it causes a balance with the same combination of filters. From the calibration curve the temperature of the standard, and hence of the lamp being measured, is read off. This arrangement will readily indicate the difference in colour of a lamp caused by 0·1 per cent. change in the voltage at its terminals.

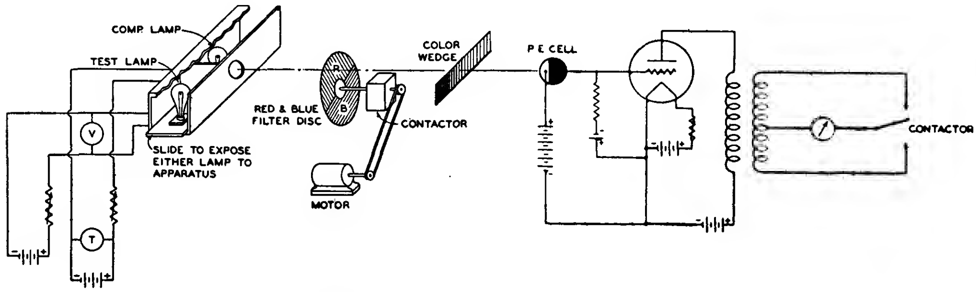

Fig. 4. Colour matching apparatus.

By attaching the colour matching apparatus to a sphere which is used also for photometric purposes, two operators can get, simultaneously, photometric measurements and colour temperature measurements. Not enough experience has been had with this apparatus in every-day use by non-scientific operators to enable the statement to be made that it is thoroughly in shape for industrial applications. However, with care, colour temperature can be measured without difficulty to a much closer degree than is possible by optical means and there is no reason to suppose that it will not prove to be adequate for industrial requirements.

§ 8. CONCLUSION

In concluding this admittedly incomplete résumé of recent progress in the application of the photo-electric cell to photometric and allied problems, the writer wishes to emphasise that, although the methods which have come under his observation are by no means perfect and introduce certain troubles and applications which are all their own, the practical results of their use have proved them to be on the whole so much superior to the optical methods, at least in connexion with the production and testing of incandescent lamps on a large scale, that the older methods are rendered obsolete. Undoubtedly the superiority of the photo-electric method will be increased as the future produces improvements in the practices and apparatus of the present day.

THE PHOTO-ELECTRIC CELL AS A PRECISION INSTRUMENT IN PHOTOMETRY

By T. H. HARRISON, B.Sc., Ph.D., A.Inst.P.,

Photometry Division, The National Physical Laboratory.

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ABSTRACT. The characteristics of photo-electric cells are discussed with reference to their application to photometry of high precision. Several faults which photo-electric cells still possess, such as dark current, variation of sensitivity with time of illumination, lack of proportionality between photo-electric current and illumination, unsuitable colour sensitivity, leakage of the photo-electric current, and unequal sensitivity over the cathode, are discussed and methods are indicated by which the effects of these can be completely eliminated.

Suggestions are given as to the features which should receive most attention in the design of photo-electric cells intended for photometric use.

§ 1. INTRODUCTION

THE fact that the photo-electric cell gives a small but easily measured electric current upon exposure to light at once indicates that its most obvious practical application is that to the measurement of light. In fact the rough estimation of fairly high illumination with the aid of the photo-electric cell could not be a simpler process: all that is required is the photo-electric cell, a dry battery of from 10 to 100 volts and a sensitive high-resistance galvanometer. With such a simple arrangement fairly self-consistent results are obtainable which lead to the belief that only a small amount of elaboration of the apparatus and a little further expenditure of care in making measurements would lead to impeccable results of precision. Within certain limits this is true, and in most cases it is not difficult in photo-electric photometry to obtain very self-consistent results. Unfortunately, however, self-consistency is not all that is required. It is also necessary to translate the results into exact measurements which will be independent of the method employed. It is here where the chief difficulty lies in photo-electric photometry, which on account of several causes is apt to contain systematic errors that from their very nature cannot be observed and remain unsuspected until either another cell with very different characteristics is employed or the results are checked visually. This paper will deal with the causes of these systematic errors, indicate what steps may be taken to obviate them, and make some suggestions concerning the design of photo-electric cells intended for photometric use.

There are six possible causes of systematic errors in photo-electric photometry and they will be discussed in turn. These are:

(1) Dark current in the cell.

(2) Variation of sensitivity with time (fatigue).

(3) Lack of proportionality between the photo-electric current and the flux of light producing it.

(4) The spectral sensitivity curve of the cell differing from that required.

(5) Leakage in the cell of the photo-electric current to earth.

(6) Variation of sensitivity over the photo-sensitive surface.

§ 2. DARK CURRENT IN THE PHOTO-ELECTRIC CELL

This is met with in nearly all cells. It is due either to faulty insulation of the glass of the bulb or to the formation on the inside wall of the bulb of a thin slightly conducting layer. If the cell is mounted on a thermionic tube base, some leakage is almost bound to occur there. In some cases the existence of some sort of electrolytic current between the leads to the electrodes is not out of the question. Ordinary soft soda glass is particularly faulty in respect of its insulating properties, and cells made with it always possess a high dark current. Hard glasses such as cobalt, borosilicate, or "Pyrex" glass appear, however, to insulate satisfactorily. When the bulbs of sodium, potassium, and rubidium cells, either evacuated or sensitised and gas-filled according to the Elster and Geitel process, are made of a satisfactorily insulating glass and designed so that the distance between the leads to the electrodes is reasonably great, the dark current can be reduced so as to be quite negligible. Caesium cells, however, made in the same way possess quite a large dark current, probably on account of the high volatility of caesium. The more recent thin-film potassium* and caesium† cells in spite of their manifold advantages over the older types unfortunately seem to possess a large dark current which is objectionable for photometric purposes, especially when one is dealing with low illuminations, when the photo-electric current may be smaller than the dark current. Unfortunately also this dark current is apt to be variable. Provided, however, that the dark current is reasonably constant and is not altogether too large, its effect can usually be eliminated. When a galvanometer is being used, for instance, readings should be taken from the zero which is obtained when the circuit is completed and the cell in darkness and not from that when the circuit is broken. This leads to no difficulties but does not allow the use of a reversing key. When valve amplification is being used, even less difficulty is encountered, for in the output circuit of the valve there is always a current which is required to be neutralised. When, for more sensitive work, an electrometer is used, the situation is rather more complicated; for in such work, where the photo-electric current is very small, the relative value of the dark current is high, usually producing an electrometer drift of such magnitude that this system of measurement becomes impracticable, unless some means is found for compensating the dark current. This can be done by using a second cell connected in series with the measuring cell and acting as a compensator to its dark current as indicated in Fig. 1. The cell C_1 is used to measure the intensity of the source S_1, while C_2, exposed to a faint illumination S_2, gives a current equal to the dark current in C_1. Obviously in this arrangement C_1 must be the cell with the larger dark

* N. R. Campbell, *Phil. Mag.* **6**, 633 (1928).

† Referred to by L. R. Koller and H. A. Breeding, *Gen. Elect. Rev.* **31**, 476 (1928) and L. R. Koller, *Journ. Opt. Soc. Amer.* **19**, 135 (1929).

current. When this arrangement is operated in the manner outlined above, the initial rate of charging of the electrometer is proportional to the flux of light affecting C_1, provided of course that this cell obeys the proportionality law. The circuit of Fig. 1 can, however, be used in a rather different manner to provide a null method of photo-electric photometry. Such a system can be used in two ways for measurements of intensities.

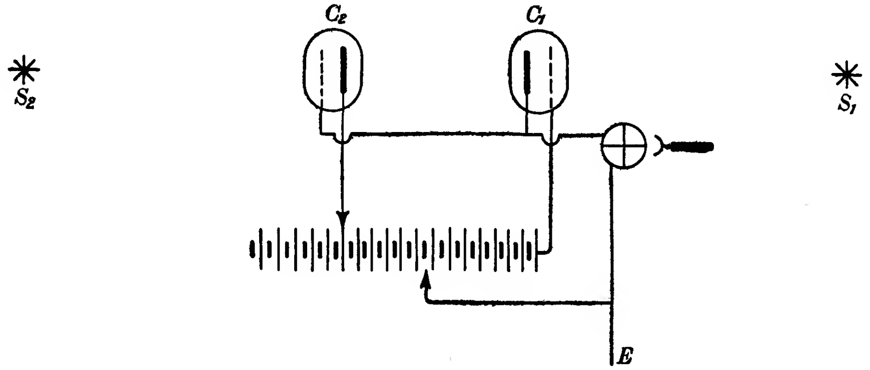


Fig. 1. Method of compensating dark current.

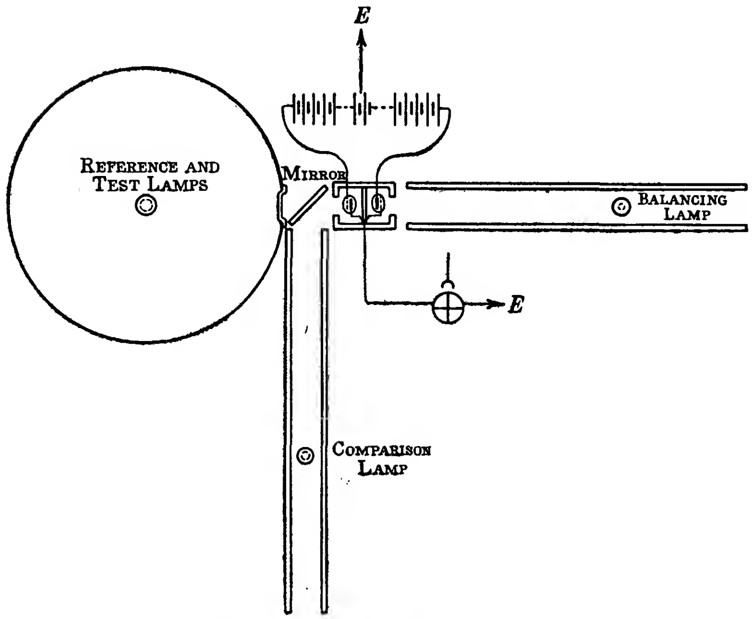


Fig. 2. Apparatus for measuring either mean spherical or directional intensities of electric lamps.

The first utilises one of the cells alone (say C_1) to give the measurements, while C_2 is used only for the purpose of compensation. An arrangement of this type at the National Physical Laboratory for measuring either mean spherical or directional intensities of electric lamps is indicated in Fig. 2. One sphere, a metre in diameter, and two photometer benches are employed. The left-hand cell is exposed to the light

from the comparison lamp after reflection by the diagonal mirror. This mirror can be slid out of the way, and then the cell is exposed to the light from the diffusing window of the sphere into which the standard lamps and those to be tested are inserted one after another. The inverse square of the optical distance of the comparison lamp from the left-hand cell, when the position of the comparison lamp on the bench is adjusted so that its effect is equal to that produced by the lamp in the sphere, is a measure of the luminous output of the lamp in the sphere. By interchanging the comparison and reference and test lamps, measurements of directional intensity are made with no change in the principles involved in the method. This arrangement completely eliminates the effects of dark current and lack of proportionality in the photo-electric cell and, in so far as the mirror can be moved in and out of position quickly, there is also complete elimination of the effects of lack of constancy in the sensitivity of the cell.

The second way of using the null method with the same bridge arrangement of two cells is the more obvious one, but it allows the intrusion of all the faults of photo-electric cells. The standard lamps and those to be tested are placed in a fixed position in front of one cell while the comparison lamp mounted on the carriage of a photometer bench illuminates the second cell. Let the illumination on the first cell from the lamp at fixed distance be E, the distance of the comparison lamp from the second cell d and its intensity I', the dark current in the first cell i_0 and that in the second cell i_0'; then for balance the current through the first cell equals that through the second, that is,

$$kE + i_0 = \frac{k'I'}{d^2} + i_0' \quad \text{and} \quad kE = \frac{k'I'}{d^2} + (i_0' - i_0).$$

Thus the intensity of the lamp to be tested is not proportional to the inverse square of the distance of the comparison lamp unless the dark currents through the two cells are equal, which can hardly ever occur unless they are both zero.

This bridge of two cells can also be used for matching the colour temperatures of electric lamps, by using two cells of different colour sensitivity or by covering one or both of them with a coloured filter*. The two cells are exposed to illumination from the same lamp, and the system is balanced by covering one of them with an adjustable aperture. The theory is based on the principle that variation in intensity of the source but without change in colour will affect both cells equally and will not affect the balance, but that variation in colour will affect the cells unequally and therefore upset the balance. But if the cells possess dark current the condition for balance is

$$kI + i_0 = k'I + i_0',$$

so that

$$I = \frac{i_0' - i_0}{k - k'}.$$

The condition to be fulfilled for this process of colour matching is that I should be indeterminate, which can only occur if i_0 and i_0' are equal when of course k and k' are also equal. Here again it is better to obtain equality by making and using cells in which the dark current is as near to zero as possible.

* N. R. Campbell, *Journ. Scient. Instr.* **2**, 177 (1924–5).

In the first system of employing the bridge null method of photo-electric cells the effect of dark current is certainly eliminated, but even there the dark current causes to the operators inconvenience and trouble when adjusting the apparatus for measuring lamps of widely different power or when readjusting after one of the cells has been changed.

§ 3. VARIATION OF SENSITIVITY WITH TIME

This is a common trouble encountered in photo-electric cells, and often referred to as "photo-electric fatigue." This term is a very unfortunate one for two reasons:

(1) Exposure to light of a photo-electric cell may not decrease its sensitivity, but for some specimens the sensitivity remains unchanged while for some others the sensitivity actually increases.

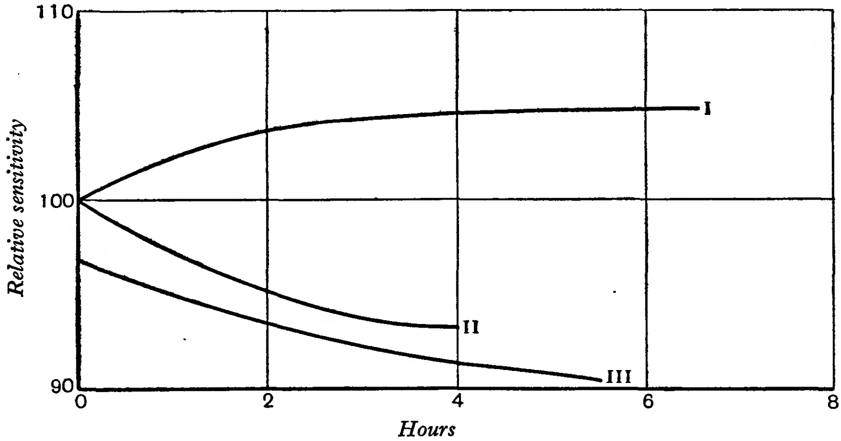


Fig. 3. Change in sensitivity with time of exposure to light.

(2) The term "photo-electric fatigue" was introduced in the early days of photo-electricity to denote the decrease in sensitivity of polished metal surfaces which were exposed to the atmosphere. The common occurrence of this sort of fatigue, obviously due to changes produced by the chemical action of the atmosphere on the metal surface, does not justify the assumption that some sort of fatigue must always occur when the sensitive surface is enclosed in an airtight vessel such as a glass bulb.

It is a fact, however, that most photo-electric cells are subject to variation in sensitivity on account of slight changes in the sensitive surface due to the action of light and the passage of the electron current. With most photo-electric cells also there are usually changes in sensitivity with temperature, for, although the photo-electric effect is independent of temperature, the effect of changes of the latter in a cell enclosed in a bulb is to vary the gas pressure and possibly to produce slight chemical actions.

The red and infra-red sensitive thin-film cells are more subject to change of sensitivity than those using the alkali metal in bulk, and Fig. 3 gives the results of

measurements on the constancy of two caesium thin-film cells, using the illumination from a 3-inch diffusing glass window of a 2 ft. 6 in. cube containing a lamp giving 232·5 lumens. These cells were both made in the same way and it is curious that the effect of illumination for one cell (Curve I) was to increase the sensitivity while for the other cell (Curves II and III) a decrease was produced. Between the two curves II and III this cell was left in darkness without any applied potential, and partial recovery took place. If the system employed in taking photometric measurements is such that this drift of sensitivity is neither compensated nor allowed for, systematic errors will certainly enter into the results, and it is clear that the position has not yet been reached where a photo-electric cell can be used as a standard of light sensitivity.

§ 4. LACK OF PROPORTIONALITY BETWEEN PHOTO-ELECTRIC CURRENT AND THE FLUX OF LIGHT PRODUCING IT

This occurs to some extent in all photo-electric cells, and it is still largely a matter of chance as to the degree to which for any particular cell the proportionality law is obeyed. For most cells, however, it is unlikely that errors greater than 1 per cent. will be introduced if the ratio of illuminations compared does not exceed two or at the most three. This degree of precision may be adequate for certain types of work, but for high-precision photometry it is impossible to rely upon the proportionality law except within a small region of illuminations. It may be as well to mention the fact that the curvature of the line showing the relation between photo-electric current and illumination may be either positive or negative, with the consequent result that reliance on the proportionality law may with different cells produce errors on each side of the true values.

§ 5. EFFECT OF THE COLOUR SENSITIVITY OF PHOTO-ELECTRIC CELLS

Until the advent of the red-sensitive thin film cells, the colour sensitivity of the eye could not be reproduced by the photo-electric cell without absorbing so much of the effective light with a coloured filter that there was an undue loss in sensitivity*. This was on account of the very small sensitivity of the thick-film cell to orange and red light. The best method of overcoming this difficulty was to effect a partial compensation with a yellow filter, the Wratten $K3$ filter being suitable†, and apply corrections from a previous calibration when the intensities of electric lamps run at different colour temperatures were to be compared. Photo-electric photometry of sources of selective coloration was quite out of the question. The application of corrections, however, and the necessity of possessing some measure of the colour temperatures of the lamps used, involved so much work and allowed the introduction of so many additional errors that photo-electric photometry was of little service except for studying variations in lamps with time and for comparing lamps which

* T. H. Harrison, *Trans. Opt. Soc.* **28**, 195 (1926–7).

† N. R. Campbell, *Journ. Scient. Instr.* **3**, 77 (1925–6).

had previously been colour-matched. Even in this latter case there seemed to be small differences between results obtained photo-electrically and those obtained visually.

The thin-film cells, although less satisfactory than the thick-film ones with regard to freedom from dark current and to constancy of sensitivity, are, however, highly sensitive throughout the whole range of the visible spectrum and the possibility of finding suitable filters to reduce the colour sensitivity curves to that of the eye to a reasonable degree of approximation and without an undue loss of sensitivity is by no means out of the question. This matter is being investigated and, although the results are not yet complete, those already obtained are very promising, and it is practically certain that, for photometric work in the visual region, the thick-film blue-sensitive cells will soon be obsolete, although they will continue to be useful for special purposes. The combination of a blue-sensitive and a red-sensitive cell connected in parallel and with an adjustable aperture in front of one of them may be

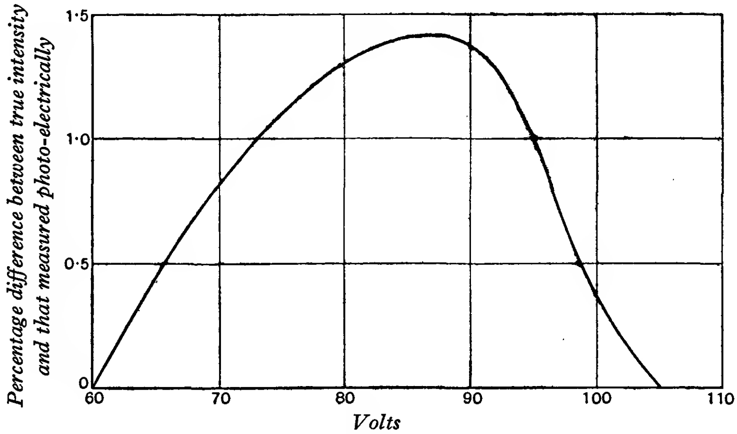


Fig. 4. Calibration curve for colour correction.

used as a combined light-sensitive device which will be neither excessively blue-sensitive nor excessively red-sensitive, and a degree of compensation may be so obtained that the intensities of an electric lamp run at widely different colour temperatures may be fairly accurately compared. On account of the fact that the colour-sensitivity curve of such a combination is very much broader than, and quite different from, that of the eye, true compensation is not possible with this arrangement. A similar but less pronounced difficulty has been experienced in the compensation of a red-sensitive cell with coloured filters. Thus for a certain cell-filter combination the calibration curve shown in Fig. 4 was obtained. If the range of colour temperatures dealt with is smaller, the accuracy of compensation can be greatly increased. But another difficulty arises from the fact that, owing to the "getter" process, the bulbs of most electric lamps have a yellow tinge which varies from lamp to lamp. This is sufficient to cause errors. For instance, results obtained with lamps made in 1911 (obviously "non-gettered") were found to be self-consistent, and some with lamps made in 1922 (gettered) were also self-consistent;

ON THE PHOTO-ELECTRIC MEASUREMENT OF DAYLIGHT

By W. R. G. ATKINS, Sc.D., F.R.S., and H. H. POOLE, Sc.D.

MS. received April 12, 1930. *Read June* 5, 1930.

ABSTRACT. For daylight photometry in most situations we have found sodium or potassium vacuum cells to be the most suitable, though their relative insensitivity to wave-lengths longer than about 5000 A.U. is a disadvantage. A new type of caesium vacuum cell, which is sensitive to the whole of the visible spectrum, has given very promising results. Gas-filled cells may be used if the light is very weak. Precautions must be taken, however, to eliminate the effects of possible changes of sensitivity during the measurements.

Owing to the wide variations that occur in the angular distribution of daylight it is desirable to mount the cell behind a diffusing surface. We have found a type of opal glass very suitable for this purpose.

Various methods of measuring the current have been used, sensitive portable galvanometers being the best where a steady support is available. For use at sea in a small vessel a potentiometer-valve-telephone method seems to be the most convenient, while for work in a small boat the flashing neon lamp may be used. Electro-chemical methods are convenient for finding the average illumination over a definite period; or a continuous record may be obtained by means of a thread recorder.

The pronounced blue-sensitivity of most cells presents certain difficulties in their standardisation. A method of standardising by means of a carbon arc is described.

A short account is given of some recent work with the new red-sensitive cell, illustrating its use to measure changes in the colour of daylight.

§ 1. INTRODUCTION

THE use of photo-electric cells for the measurement of daylight* is of growing importance in connexion with problems concerning photo-synthesis and plant growth. As it involves problems which differ somewhat from those met with in the photometry of artificial lights, the following notes may be of some service to those who wish to make use of this method.

* See H. H. Poole, "On the photo-electric measurement of submarine illumination," *Scient. Proc. Roy. Dublin Soc.* **18**, 99–115 (1925).

H. H. Poole and W. R. G. Atkins, "On the penetration of light into sea water," *Journ. Marine Biol. Assoc.* **14**, 177–98 (1926).

—— —— "Further photo-electric measurements of the penetration of light into sea water," *ibid.* **15**, 455–83 (1928).

—— —— "Photo-electric measurements of submarine illumination throughout the year," *ibid.* **16**, 297–324 (1929).

W. R. G. Atkins and H. H. Poole, "The integration of light by photo-electrolysis," *Scient. Proc. Roy. Dublin Soc.* **19**, No. 16, 159–64 (Jan. 1929).

—— —— "Methods for the photo-electric and photo-chemical measurement of daylight," *Report of Conference of Empire Meteorologists, Agric. Sect.* 67–89 (1929); *Biol. Rev.* **5**, No. 2, 91–113 (1930).

—— —— "The photo-electric recording of daylight," *Nature*, **125**, 305 (1930).

has a larger sensitivity than the former even when the infra-red is absorbed with a suitable filter. Since, as has already been pointed out, the use of large lenses to collect the light is not free from objections in photo-electric photometry, it is desirable for the sake of sensitivity that the photo-electric cells employed should be of a reasonably large size. The most suitable size of the sensitive surface is about 4 sq. in. This is the same size as the white screens of the Lummer-Brodhun photometer. Larger sizes of cells would lead to the difficulty in the measurement of directional intensities arising from the fact that the light from the lamp to the large cell would be insufficiently uni-directional. The larger electrical capacities of such cells would also diminish the extra sensitivity obtained if electrometer or thermionic tube methods were used to detect the current. Since it is desired to know the exact position of the sensitive surface of the photo-electric cell in order to measure the distance of the centre of the light source from it, it is desirable that this sensitive surface should be formed on a flat plate. The practice of mounting photo-electric cells on thermionic valve bases, which is becoming rather frequent, is undesirable for cells designed for photometry on account of electrical leakage, although there is no objection if only one of the electrodes is connected through the base while the other passes through the bulb some distance from the former in the manner of the fifth lead to a pentode thermionic tube.

I should like to express my thanks to Messrs L. H. McDermott and C. J. MacManus for assistance in the preparation of this paper.

§ 7. VARIATION OF SENSITIVITY OVER THE PHOTO-SENSITIVE SURFACE

For certain purposes in photo-electric photometry it may be desired to use a lens system for the purpose of

(1) collecting a large flux of light and causing this to converge upon a small photo-electric cathode,

or (2) forming an entrance pupil to the cell, from which the exact distance of the light source can be measured.

The effect of such a lens system will be to produce an image of the lamp filament on the sensitive cathode of the cell. In such a case, small differences in the position of lamp filaments lead to differences in position and shape of the light image in the cell, with the result that different areas of the sensitive surface are being used to produce the photo-electric emission. The sensitivity over the cathode of a photo-electric cell is never perfectly uniform, the lack of uniformity being naturally more pronounced in the red and infra-red cells with thin layers of the active substance, so that, in measuring a batch of lamps, some of them with rather different filament positions give results different from their true value. Since the production of photo-electric cells with a cathode of perfectly uniform sensitivity is, if not impossible, at any rate uncertain, this method of using a lens system should usually be avoided. It may also be taken as a general principle that a photo-electric cell will be most satisfactorily operated when the whole of the light-sensitive surface or a large portion of it is exposed to a uniform illumination. If this is to be arranged, and at the same time it is also desired to use a large lens for the purpose of collecting the light, a diffusing glass must be introduced somewhere in the system. This entails a considerable loss of intensity of light if the diffusing glass is placed in a position where it will be most effective, and when everything is taken into account there appears to be no advantage in the use of the lens and diffusing glass system in high precision photo-electric photometry. The illumination from electric lamps placed over 0·5 m. from a photo-electric cell is sufficiently uniform over the cathode of the cell that differences in the design of the filaments and in the exact positioning of the lamps do not lead to any errors arising from lack of uniformity of sensitiveness over the cathode.

§ 8. DESIGN OF PHOTO-ELECTRIC CELLS FOR PHOTOMETRIC USE

The ideal cell for accurate photometric work must fulfil conditions which are unnecessary for those designed for the operation of relay circuits or for certain technical purposes, such as sound reproducing. It should be free from dark current even if this can only be obtained by leading one of the electrode connexions through a rather clumsy side tube for the purpose of adequate insulation. It must possess a sensitivity which is high throughout the whole visible spectrum in order that, with a colour filter, the colour sensitivity of the eye can be reproduced. For this purpose the thin-film potassium or the thin-film caesium cells must be used. The former possesses a colour sensitivity more nearly similar to that of the eye, but the latter

but a comparison of the two sets of results showed a discrepancy of 1·1 per cent. This was found to be due to the fact that, although the photo-electric photometer had been compensated so that it would measure accurately sources of different colour temperatures, the selective coloration of the "gettered" bulbs was sufficient to produce the discrepancy. It is necessary, therefore, in photo-electric photometry to seek for a photo-electric cell and filter combination which will reproduce the visual colour sensitivity of the eye: a colour sensitivity which appears to give satisfactory results but which differs from that of the eye will undoubtedly lead to systematic errors which may remain unsuspected for a long time.

§ 6. LEAKAGE OF PHOTO-ELECTRIC CURRENT TO EARTH

This is generally associated with high values of the dark current and occurs when the cell possesses an earthed guard-ring. When the photo-electric current is measured with a galvanometer or with the aid of thermionic valves, this leakage is not disadvantageous since it is always very small in comparison with the current passing through the galvanometer or through the grid leak of the thermionic valve but, when an electrometer or electroscope is used, the leakage has the effect of considerably reducing the sensitivity obtainable. For measurements where the highest sensitivity is required, it is therefore desirable to avoid the use of photo-electric cells which allow this leak to earth. When using a bridge of two gas-filled cells with an electrometer to measure the difference between the currents through the two cells, there is another effect which may be confused with leakage to earth in that it also makes the electrometer behave like a galvanometer since it moves to a given deflection and remains there instead of charging up indefinitely at a uniform rate. This effect is the outcome of the fact that the sensitivity of gas-filled cells is dependent upon the applied voltage. What actually occurs is this: the illuminations on the two cells are adjusted so that the current through one of them slightly exceeds that through the other when the electrometer is earthed. When the electrometer key is released, the pair of quadrants connected to the photo-electric cell system are gradually charged by the difference between the two currents. This charging of the electrometer leads to a decrease in the potential applied to the cell yielding the larger current and an increase in that applied to the cell which gives the smaller current. The change in potential applied to the cells involves—with gas-filled cells—a change in the photo-electric sensitivity in the same direction, with the result that at a certain electrometer deflection there will cease to be any difference between the two photo-electric currents. Beyond this point, which depends upon the original difference between the currents, the electrometer will not deflect, with the result that the behaviour of the electrometer is very similar to that of a galvanometer. This effect limits very considerably the sensitivity of the electrometer system of measuring photo-electric currents.

The work is generally facilitated by the fact that the illumination to be measured is large, and great accuracy is seldom needed. On the other hand, the range to be covered may be very great, say from 5 to 150,000 metre-candles, as in our marine work, and allowance must be made for the fact that the angular distribution of the light is very variable, and that the colour is very different from any of the usual standards. Moreover, for work in the field, portability of apparatus is essential, while for marine work the apparatus used to measure the current must not be affected by the motion of the ship, which is often violent. It is also highly desirable that a method which is essentially to be employed for routine measurements should involve the simplest possible operations.

In designing an outfit for any particular purpose we have to consider (*a*) the type of photo-electric cell to be used, (*b*) the photometer in which it is to be mounted, (*c*) the method to be adopted for measuring the photo-electric current, and (*d*) the method of standardisation to be used.

§ 2. TYPES OF PHOTO-ELECTRIC CELL

Vacuum cells are amply sensitive for many purposes and, where this is the case, should always be used, as their reliability and constancy render them far superior to any gas-filled cell that we have tried. Comparatively large cells can generally be used with advantage as these are, naturally, more sensitive to a given illumination. We have found vacuum sodium cells made by Dr R. C. Burt, of Pasadena, very useful for many purposes. These cells are made by electrolysis of the glass of the cell wall. They are about the size of a 60-watt gas-filled lamp, and are mounted in sockets similar to those used for wireless valves. The sensitivity varies somewhat from cell to cell. We have one in use which, when mounted behind opal glass, gives a current of one microampere with an illumination of about 800 metre-candles, the anode potential being 60 volts. These cells have little, if any, sensitivity to wave-lengths longer than about 5000 Å.U., which is a disadvantage for most purposes, so that it is often better to use a potassium cell, which has some sensitivity in the green. We have had several of these cells, kindly made for us at the General Electric Company's Research Laboratories, in use for some years and have never detected any changes in their sensitivities. A small one, which we frequently use as a standard of comparison for other cells, and for measuring daylight in open sites, gives about 1 μA. for 40,000 m.c.

We have recently been supplied by the General Electric Company with a new type of vacuum cell containing an oxidised silver kathode covered with a thin film of caesium (type CMV 6). This cell possesses the great advantage of red sensitivity. Measurements with this are given further on.

In certain situations, e.g. at depths greater than about 30 metres below the surface of the sea, the light is too weak to be readily measured with a vacuum cell of reasonable size. For submarine work at these depths we have found gas-filled potassium cells satisfactory, provided that suitable precautions are taken in their use. The method which we have adopted consists in comparing the readings for the gas-filled cell, supplied with an anode potential of only a few volts, with that for a vacuum potassium cell exposed beside it on the deck both before and after the

series of submarine readings. Allowance can then be made for any slow variation of sensitivity that may have been in progress during the series. It is necessary to use quite small anode potentials for such cells when exposed to full daylight, as otherwise the current might exceed the limit (which varies from cell to cell) beyond which it is no longer proportional to the light, or might even reach the glow point. When a depth has been attained at which the light is so much reduced that an increase in sensitivity is needed, this is obtained by increasing the anode potential (up to a limit of 120 volts in our work). The relative sensitivities at the different anode potentials used must be found by comparison each time that a change is made. In this way we have found it possible to measure illuminations down to a few metre-candles, even with the rather small window fitted to our submarine photometer.

§ 3. MOUNTING OF CELLS

The cell must obviously be mounted in some kind of case which, for submarine work, must be watertight and capable of standing pressures up to at least 8 or 10 atmospheres. High tension ignition cables are very suitable for leads, the joints where they enter the photometer case being made water-tight by rubber-packed screw glands. For shore work it is generally sufficient to make the case rainproof and attach the cables firmly to the case, so as to protect the terminals of the cell from all strains. The best possible insulation is of course necessary.

It is generally advisable to mount the cell behind a window made of some translucent but diffusing material, so that the reading may be proportional to the illumination on some definite plane, which may be horizontal, vertical, or oblique according to the setting of the photometer. If the diffusing properties of the window are sufficiently good, the reading of a photometer with a horizontal window will be proportional to the vertical illumination at the given point, no matter what the actual distribution of the light may be. If the diffusing window is omitted the reading will generally depend in a complex way, which will be different for every cell, on the angular distribution of the light, both in altitude and in azimuth. The best diffusing material that we have found so far is a thin glass opalised on both surfaces, supplied by Messrs J. Hetley & Co., 35 Soho Square, London. The effect of this glass is generally to reduce the light recorded by the cell to about one-half without greatly affecting the relative sensitivity of the photometer to the different parts of the visible spectrum to which the cell is sensitive. It is evident that a matt front surface to the window would lose the greater part of its diffusing properties if it were wet. This glass has a polished front surface so that its properties are not so affected. If necessary a small allowance may be made for the effect of obliquity of illumination in increasing the reflection losses at the front surface. In making this allowance, which seldom exceeds a few per cent., the relative effects of direct sunlight (of which the altitude is known) and diffuse skylight may be found by taking alternate readings with and without the interposition of a small object at a distance of a few feet from the window so as to shade off the sun. The ratio of the unshaded and shaded readings forms a useful index of the relative brightness of the direct sunlight.

Another small correction may be desirable in marine work to allow for the fact that the reflection loss at a water-glass surface is less than that at an air-glass surface. This is only worth considering when dealing with the question of the amount of light cut off by the surface of the sea. It is worth noting in this connexion that, if a curved window be employed or if a bare cell be used, refraction at the surface will reduce the light entering the cell when it is submerged, so that an exaggerated estimate will be formed of the light cut off by the sea surface.

It is generally convenient to work with the window horizontal, so as to measure the vertical illumination, but in some situations, e.g. indoors or under trees, it may be desirable to measure the horizontal illumination in some definite azimuth, or the surface may be set by trial to catch the maximum illumination. Measurements of the horizontal illumination under water are also useful, as their comparison with the vertical illuminations at the same depths gives information as to the angular distribution of the light.

A knowledge of this distribution is necessary if we wish to deduce the total illumination at a given point from the measured vertical illumination. This total illumination is probably the factor of importance in photo-synthesis. It can be directly measured by means of a photometer whose absorbing surface is a complete sphere, but it is not easy to arrange a photo-electric cell in such a mounting. In this respect a photo-chemical method has an advantage, as it is easy to expose the sensitive liquid in a spherical flask.

§4. MEASUREMENT OF THE PHOTO-ELECTRIC CURRENT

The current to be measured is often so large that a portable galvanometer or even a microammeter may be used. For such cases, if a steady support is available for the galvanometer, no other method need be considered. We have found galvanometers and microammeters of the Onwood type (Gambrell) very suitable, and also a small mirror galvanometer made by Messrs Tinsley, in which the lamp and scale are included in the box containing the galvanometer. This gives a deflection of about 12 scale divisions per μA, which may be doubled by means of a reversing key. For very weak light a much more sensitive Onwood mirror galvanometer, giving about 500 scale divisions per μA has been used, but this is, naturally, more troublesome to set up out of doors, though since the coil is suspended from its centre accurate levelling is not necessary. For strong lights with sensitive cells we have found Onwood microammeters amply sensitive; in fact it is often necessary to reduce the sensitivity by means of shunts. A high tension battery as used for wireless reception forms a convenient source of pressure. The interposition of a safety resistance of not less than 10,000 ohms is advisable with vacuum cells to protect the high tension battery, and essential with gas-filled cells to protect the cell itself.

A continuous record of the light may be made by the use of a recording galvanometer, such as the Cambridge Instrument Company's thread recorder. Such records are at present being obtained in the Marine Biological Laboratory at Plymouth, a watertight photometer being exposed on the roof. Continuous exposure of the

cell to full daylight is evidently a severe test of its constancy, but we think that vacuum cells will be found to be satisfactory for this purpose. The constancy of the photometer is checked periodically.

For measuring the time-integral of the illumination over a period such as a day, the current may be passed through a small copper voltameter, and the copper deposited on the platinum kathode, dissolved off, and estimated colorimetrically. For shorter periods the acid or alkali produced may be estimated. Segelken* has since used a gas-filled caesium cell, the current from which was amplified, to produce hydrogen electrolytically. The combination obviously cannot give quantitative results.

No form of sensitive galvanometer (except, possibly, a string galvanometer) is suitable for use at sea in a small vessel. For marine work we have always employed the rather obvious method of passing the current through a 100,000 ohm resistance, and balancing the P.D. between the ends against a potentiometer reading directly to 10^{-4} volt, using a telephone as a null-point detector. This necessitates the use of an interrupter in the detector circuit. For this purpose the best arrangement that we have tried so far consists of a smooth metal wheel rolling lightly on a toothed metal wheel, which is rotated by clock-work, the current being made to flow from wheel to wheel. The use of a clock spring involves frequent winding, but it is not easy to devise any compact electrically driven interrupter that does not cause induced currents, which render a balance impossible.

The simple arrangement outlined above would not, however, be sufficiently sensitive, so a two-stage valve amplifier is introduced between the interrupter and the telephone. The method thus possesses the advantage of sensitivity due to valve amplification without the drawback inherent in so many valve methods that uniformity of amplification is necessary. It is not necessary, for instance, to take elaborate precautions to ensure that the valves are always run at exactly the same temperature.

The sensitivity is also increased by the use of a condenser of about $1\,\mu$F in parallel with the interrupter and the input circuit of the amplifier. When the potentials are not balanced this condenser charges up during the intervals when the interrupter circuit is broken, and discharges again when this circuit is closed.

With this apparatus it is easy to measure steady currents to within 10^{-9} ampere under good conditions. As might be expected, the chief difficulty is the elimination of leakage currents when the air is very damp, as it often is at sea. By paying special attention to the lay-out of the circuits, and by the use of suitable guard surfaces to intercept any leakage currents from the high tension batteries, it has been found possible to use the apparatus satisfactorily throughout the year under all but the most adverse atmospheric conditions.

For measuring the average value of a very variable illumination such as generally exists just beneath the surface of the sea, the potentiometer method is not very suitable, owing to the difficulty of obtaining a balance. For this purpose, and for

* J. G. Segelken, "The determination of light intensity," *Ecology*, **30**, 294–7 (July, 1929).

use in small boats on inland waters, the most promising method of measurement appears to be that of the neon lamp photometer, as suggested by Dr J. H. J. Poole* and described in another paper†.

§ 5. STANDARDISATION OF PHOTOMETERS

In many applications of daylight photometry the absolute values of the illuminations recorded are of much less importance than their ratios. Absolute values are, however, often required and, if so, it is necessary to calibrate one at least of the photometers to be used. Unfortunately, most photo-electric cells differ so much from the eye in their colour sensitivity that, if an incandescent lamp is used as a standard of comparison, the great relative sensitivity of the cell to blue light will give values for daylight illumination far in excess of those found by visual means. Moreover, in order that the results should be in any way comparable with those obtained by other workers, it would be necessary to specify precisely at what "efficiency," i.e. at what temperature, the standard lamp was run. Special "daylight" lamps, run at a carefully adjusted voltage, may be used, or the daylight reading of the photometer may be compared with a simultaneous visual measurement made by some such instrument as the Macbeth Illuminometer (which has been used for this purpose by Shelford and Gail‡), but in the latter case the scale so found would vary appreciably according to the quality of the daylight at the time of the comparison.

There is, accordingly, a good deal to be said in favour of the use of an open carbon arc as a source for comparison, in spite of its tendency to unsteadiness. It is, at least, a source which can readily be reproduced by other workers, and with good quality carbons burning silently under normal conditions the temperature of the glowing crater and, hence, the colour of the light will be very approximately constant. The carbons should be mounted vertically, the positive being above, and a magnified image of the arc should be projected horizontally on to a vertical screen. It is, then, easy to ensure that the crater is in a definite position, that its rim is horizontal, and that the arc is sufficiently long to prevent the shadow of the negative carbon from falling on the photometer. The line from the crater to the centre of the photometer window may conveniently be arranged at 45° to the vertical, the window being perpendicular to this line at a distance of some 20 cm. from the crater.

Combining the results of Forrest§ with those of Allen||, we find that the candle-power of the arc should be 232 per ampere in a direction normal to the plane of the crater rim, or 164 per ampere at 45°, at which angle no shadow need be cast by the

* J. H. J. Poole, "A simple form of photo-electric photometer, using a neon lamp to measure the current," *Scient. Proc. Roy. Dublin Soc.* **19** (N.S.), No. 3, 17–25 (1928).

† J. H. J. Poole and H. H. Poole, "The neon discharge tube photometer," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 142 (1930).

‡ V. E. Shelford and F. W. Gail, "A study of light penetration into sea water made with the Kunz photo-electric cell," *Publ. Puget Sound Biol. Sta.* **3**, No. 65, 141–76 (1922).

§ J. F. Forrest, "The electric arc as a standard," *Electrician*, **71**, 729, 1007 (1913).

|| N. A. Allen, "The current density in the crater of the carbon arc," *Proc. Phys. Soc.* **33**, 62–9 (1921).

negative carbon. We have used solid carbons 7 mm. in diameter, the current, usually 6 to 7 amperes, being read on a good ammeter at the same time that the photo-electric current is measured. Our experience with this method would seem to show that, if in each calibration the mean of several readings is taken, successive calibrations with different carbons ought to agree to within a few per cent. The chief source of error is probably the difficulty of ensuring that the crater rim is horizontal, so that the angle of illumination is accurately 45°, as assumed.

If, as our recent experience leads us to hope, the new red-sensitive cells prove to be quite reliable, it will be possible to use them with a colour filter such as to render them very similar to the eye in relative colour sensitivity. Such a photometer could evidently be standardised against an incandescent lamp.

The most convenient source for checking the constancy of the photometers is a small vacuum lamp mounted inside a bell-shaped vessel, which can be placed on the photometer so as to exclude all light except that of the lamp. This should be run at some definite voltage, well below its rated voltage, so that, with the very short periods for which it is in use, its candle-power may remain constant for years.

In practice it has been found most convenient to reserve one or more vacuum cells as sub-standards, which are periodically tested with the test lamp in the laboratory, and to have others for field use. These are cross-checked against each other and against the sub-standard. These vacuum cells have remained remarkably constant, except for the one used in permanent recording which has shown a decline in sensitivity followed by an increase. The source of this change, which is about 30 per cent., has not so far been located. The increase may, possibly, be due to partial removal by weathering of the opalised surface of the glass. It seems preferable to continue to keep the cell in use, and to rely upon more frequent calibrations against a similar, but unexposed, sodium cell.

§ 6. THE WORK OF KUNZ AND SHELFORD

These workers* use gas-filled cells for recording and appear to have obtained a greater measure of constancy in their performance than we have ever experienced with this type of cell. Nevertheless, we see no reason to abandon the vacuum type where illumination is adequate. In preference to the use of a diffusing surface they have sought so to design the form of the cell that a linear relation (tested by a sector disc) between intensity and current could be obtained in full daylight, including sunlight, irrespective of the sun's altitude. For this purpose they have found a collapsed sphere type of cell to be suitable. Even this form will not accurately measure

* V. E. Shelford and J. Kunz, "The use of photo-electric cells of different alkali metals and color screens in the measurement of light penetration into water," *Trans. Wisconsin Acad.* **22**, 283–98 (1926).

—— —— "Use of photo-electric cells for light measurement in ecological work," *Ecology*, **10**, No. 3, 298–311 (1929).

V. E. Shelford, "The penetration of light into Puget Sound waters as measured with gas-filled photoelectric cells and ray filters," *Publ. Puget Sound Biol. Sta.* **7**, 151–68 (1929).

J. Kunz and V. E. Shelford, "Forms of gas-filled photoelectric cells, their properties and calibration," *Rev. Scient. Instr.* **1**, No. 2, 106–17 (1930).

the total intensity of the light. To avoid overheating they spray the lower (concave) side of the cell with water, while between the upper (convex) surface and a coloured light filter, similar in form, a blast of dry air prevents condensation. By using sodium, potassium, rubidium, and caesium cells with light filters they have been able to measure the variation in the shorter wave-lengths in air and under water, but none of the cells used were satisfactory for the red. Their records for variation in colour of light throughout the day appear to be associated with the forms of the cells used, their collapsed sphere type being the only one they regard as satisfactory.

§7. MEASUREMENTS WITH RED-SENSITIVE CELLS

Through the courtesy of the General Electric Company we have been provided with red-sensitive cells prepared by Dr N. R. Campbell. The first one, potassium on oxidised copper, soon lost its red sensitivity and was exchanged for the improved type with palladium side tube for admission of hydrogen. This was admirably red-sensitive, but in course of time the necessity for adding hydrogen became apparent—and after a period of idleness the cell became similar in colour sensitivity to an ordinary potassium cell. As we required the cell for submarine use in a water-tight vessel, the necessity of periodical re-openings was one to be avoided if possible. Fortunately Dr Campbell's newer type CMV 6 (caesium monatomic vacuum No. 6) appears to be an approximation to perfection, so far as our wants are concerned. In spite of the instability of the ordinary caesium cells, associated with the relatively high vapour pressure of this metal, the cell appears to be of great stability, and for a given sensitised area its sensitivity is far greater than that of the Burt cells. Actually, when the aperture admitting light was limited, so as to confine the illumination to that portion of the sensitised plate (see Campbell and Ritchie*, frontispiece, type C) marked as giving the best colour sensitivity, it was found that its sensitivity was slightly greater than one of the less sensitive Burt cells of far larger area, when compared on a sunny day (September 18, 1929) with blue sky and some white clouds. Thus at noon, 2, and 3 p.m. the ratios were 1·10, 1·095, and 1·03 respectively. Shielded from the direct sun, with intense blue sky and a few clouds, the ratio varied from 0·713 at 5 p.m. to 0·783 at 5.40, 0·738 at 5.50, and 0·773 at 6 G.M.T. with low haze and some pink clouds, just after sunset on September 24. This variation does not denote lack of constancy, but is due to the fact that the blue-sensitive Burt cell is relatively more sensitive to sky light than to sunlight. Against another Burt cell on September 19 with grey sky the CMV 6 gave the ratios 0·3890 and 0·3895 at 1.35 and 2.15 G.M.T. respectively. The cells were at 60 volts anode potential in every case.

§8. VARIATIONS IN THE COLOUR OF DAYLIGHT

Comparisons were made of the readings of this cell with an opal glass window, when exposed behind red, yellow, green, and blue colour filters under different conditions of daylight illumination. The transmission curves of the screens for various wave-lengths were found with a Moll vacuum thermopile, and will be

* N. R. Campbell and D. Ritchie, *Photoelectric Cells* (Sir Isaac Pitman & Sons, Ltd., 1929).

considered in a later paper. The colour sensitivity curve of the cell used appears to be similar to type 2, Fig. 7, p. 36, given by Campbell and Ritchie*. We selected the ratio for the blue screen as unity—since all our previous work had been done with blue-sensitive cells—and found its ratio to the values given with the green, yellow, and red filters. The resulting figures given in the accompanying table are arbitrary values—depending upon the colour sensitivity of the cell and upon the transmissions of the filters used—but show clearly, in a qualitative way, the variations in the colour of the light.

Table: Ratios of the currents given by a CMV 6 photo-electric cell with various colour filters in position, over opal in each case, taking the blue filter transmission as unity.

Date	G.M.T.	Place and conditions	*Red* Blue	*Yellow* Blue	*Green* Blue
Sept. 18	10.40–11.45	Laboratory roof, sun, blue sky	1·53	1·55	0·11
Sept. 19	1.50– 2.15	Antony, open site on lawn, grey sky, sun obscured	1·61	1·55	0·11
Sept. 24	3.45–·4.0	Do. blue sky, sun behind trees	0·79	0·91	0·097
Sept. 25	2.50– 3.15	Do.	0·88	1·05	0·11

It will be observed that the grey light on a cloudy day was apparently slightly redder than the mixture of sunlight and blue sky light, while the north light from a blue sky was very much bluer. The quantitative interpretation of the results is, however, somewhat complex, involving, as it does, not only the transmission curves for the screens for normal incidence, and the sensitivity curve of the cell, but also a knowledge of the angular distribution of the daylight, since the transmission curves of the screens are considerably affected thereby.

We may, however, regard the relative transmissions of the screens as convenient indexes of the quality of the light. Thus, if we take the mean of the first two lines as representing "white" light, and assign a value 100 to the proportion of such light transmitted by each screen, we find that the figures for north light on September 24 are red 50, yellow 59, green 88, blue 100; and on September 25, red 56, yellow 68, green 100, blue 100.

It is obvious that the use of such a cell renders possible a much closer accord between the visual and the photo-electric measurement of daylight. The unscreened red-sensitive cell would give too high a value to the luminosity of gas-filled electric lamps, because of its great sensitivity to red and the shorter infra-red as compared with green, to which the eye is most sensitive. Conversely, the blue-sensitive cells available heretofore would over-rate daylight if standardised on a gas-filled lamp basis, so that, for them, the carbon arc standardisation was preferable. One can now, however, compare the various light sources with the CMV 6 type cell and suitable filters, and calibrate the less expensive blue-sensitive cells against a standardised type CMV 6 in daylight. For general work it is most convenient to accept diffuse light from a grey sky as constituting white light—except, perhaps, as regards the ultra-violet. The Seventh International Photographic Congress has, however,

* N. R. Campbell and D. Ritchie, *loc. cit.*

adopted as a unit of illumination one metre-candle of mean noon sunshine, as defined by Abbot's values for spectral energy distribution at Washington, and has given methods for obtaining light of such a quality. It would probably be best to accept this standard by which to calibrate photo-electric cells used for daylight measurement in various parts of the world. As far as can be judged from the preliminary note in *Nature*, it seems that Teegan and Rendall* in Rangoon standardised their cell against a gas-filled lamp, which would rate sunlight far too high with a blue-sensitive cell.

A microammeter suffices for obtaining the colour ratios in daylight, but in greatly reduced light in a wood the more sensitive Onwood galvanometer with scale at 1 metre distance had to be used, both being housed in a box with a handle and an external coil-clamping arrangement. Even a moderate breeze introduces vibration, however, and, for general use, J. H. J. Poole's neon lamp photometer would appear more convenient; the figures for September 25 were obtained by its aid.

This paper does not purport to be a review of other people's work, but rather to give a general account of our own experience in daylight photometry. Reference may, however, be made to the prolonged series of measurements of ultra-violet and general daylight carried out by Dorno†. A review of the medical aspect of the subject has recently been given by E. M. Luce Clausen‡.

* J. A. C. Teegan and G. R. Rendall, "Integration of sunlight in the tropics," *Nature*, **125**, 447 (1930).

† C. Dorno, "Progress in radiation measurements," *Monthly Weather Rev. U.S.A.* **50**, 515–21 (1922).
—— "Zur Technik der Sonnenstrahlungsmessungen in einzelnen Spektralbezirken," *Meteorolog. Z.* pp. 234–48 (Sept. 1924).
—— "Ausstattung modernen Strahlungsobservatorien," *ibid.* **9** (1926).
—— "Tägliche, jährliche und säkulare Schwankungen der Sonnenstrahlung in Davos," *Conf. internat. de la Lumière, Lausanne-Leysin*, p. 36 (1928).
C. Dorno and F. Lindholm, "Helligkeitsverteilung über den Himmel im Ultraviolett," *Meteorolog. Z.* pp. 281–92 (Aug. 1929).

‡ E. M. Luce Clausen, "The therapeutic value of radiation," *Medicine*, **8**, No. 4, 419–71 (1929).

A PHOTO-ELECTRIC INTEGRATING PHOTOMETER

By A. S. G. HILL, B.Sc.

MS. received, June 26, 1930.

ABSTRACT. The paper describes an application of the photo-electric cell as a means of measuring the illumination from a Bennett integrating photometer, and illustrations of its use are given.

§ 1. INTRODUCTION

IN the present discussion several papers stress the need for a simple integrating photometer for the photo-electric measurement of daylight. As this subject has a wide field of interest, involving, as it does, problems of visibility, natural illumination of buildings, and biological research, the following method may be of interest to those concerned in such work.

According to Atkins and Poole*, the total amount of light arriving at a point on the earth's surface is probably the factor of importance in photo-synthesis. The correlation between the measurement of daylight illumination at any point and the simultaneous value of sky brightness introduces considerable uncertainties owing to the non-uniformity of the sky brightness on most days, and the method of deducing the total illumination at a point from the angular distribution of light and measurements of vertical and horizontal illuminations is inconvenient.

A simple integrating photometer, designed by M. G. Bennett† to measure the total amount of light arriving at a point on the earth's surface, from the sun and sky, irrespective of the position of the sun or of the distribution of cloud, embodies a measuring system of optical wedge filters and a comparison lamp. By substituting a photo-electric cell in the place of this measuring system, a simple photo-electric integrating photometer is obtained.

§ 2. DESCRIPTION OF PHOTOMETER

An experimental form of the photometer is shown in Figs. 1 and 2. The novel feature of Bennett's photometer is the light-integrating device. It consists of two opal glass bulbs A and B (Fig. 2) with polished outer surfaces, held symmetrically about a vertical axis by a brass holder C. The neck of the bulb B extends below the holder, which projects into a light-tight case and is secured by means of a flange. The photo-electric cell P is mounted on an adjustable holder and placed immediately beneath the neck of bulb B. The intensity of illumination of the polar cap of bulb B, the light from which is incident on the photo-electric cell, is measured by means of the cell.

* W. R. G. Atkins and H. H. Poole, *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 128 (1930).

† M. G. Bennett, *Proc. Phys. Soc.* **40**, 316 (1928).

It has been found experimentally that, for bulbs of given size and material, it is possible to find a position of B relative to A such that the brightness of the area in question is independent of the angular distribution of incident light. Thus, if A receives light from all quarters of the sky, the brightness of this polar cap will be proportional to the total intensity of the incident light irrespective of its distribution.

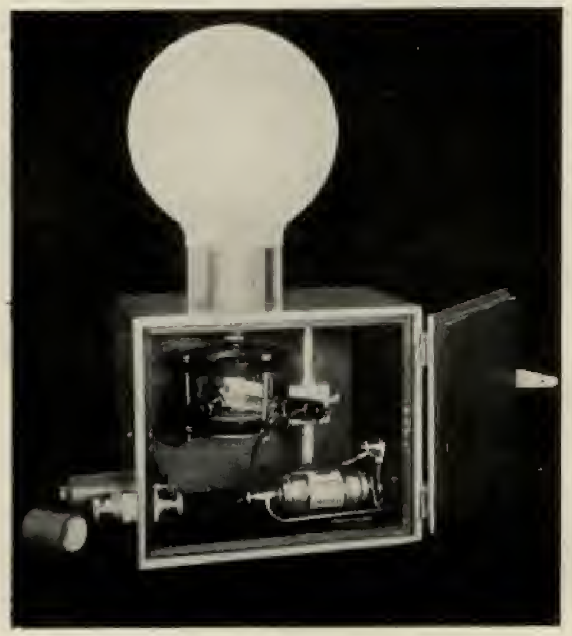


Fig. 1. Photograph of photometer.

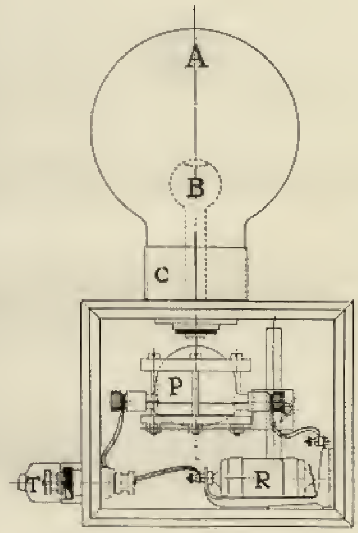


Fig. 2. Sectional drawing of photometer.

The terminals of the cell are connected to marble insulated terminals T, with a high resistance R (50,000 Ω) in series with the anode. Well insulated cable leads pass through Bakelite weather covers which screw over the terminals, thus making the instrument weather proof. The instrument is connected to a source of potential and a measuring instrument in the usual circuit.

§ 3. APPLICATION AND GENERAL CONSIDERATION

The use of the photo-electric cell involves all the uncertainties of heterochromatic photometry, but with the recent advancement in manufacturing technique it is now possible to obtain photo-electric cells such that, with the use of appropriate colour filters, a general colour-sensitivity almost identical with that of the human eye may be obtained*.

As an example of the use of the photometer, Fig. 3 A is a photograph of a record obtained in February last, using a potassium hydride neon-filled cell in conjunction with a Cambridge Instrument Company's thread recorder. The photometer was

* T. H. Harrison, *Nature*, May 10, 1930.

placed in the vicinity of a laboratory window, facing south, and a potential chosen to give a full-scale deflection (5 microamps.) for the maximum intensity of illumination at noon. Figs. 3 *B* and *C* are similar records obtained with yellow and red filters respectively on various days.

No attempt has been made to calibrate the instrument, but for its use as a simple sunshine or daylight recorder an illuminometer or arc calibration* could easily be made, and the time-integral of illumination derived from the records.

Fig. 3. Records obtained with photometer.

In order that the cell sensitivity should remain constant it is essential that as low a voltage as possible should be employed. It is thus advantageous to use large opal bulbs, with the cross-sectional area of illumination on the cell as large as possible, together with a suitable cell.

For accurate determinations of the intensity of light of specified wave-lengths, using monochromatic filters, the current obtained is usually too small to be

* W. R. G. Atkins and H. H. Poole, *loc. cit.*

registered on a thread recorder or microammeter. Photographic recording such as used by T. H. Harrison*, recording electrometers, or potentiometers may be employed or direct measurements on sensitive high-resistance galvanometers obtained. Valve amplification could be employed.

Allowance must be made for the dark current of the cell, but for a well-constructed cell this is usually negligible. The proportionality existing between illumination and the photo-electric current will depend on the type of cell employed. Generally speaking, a vacuum type is to be preferred but, with precautions, a gas-filled cell may be used. The cell must be calibrated frequently, as change of sensitivity with duration of exposure to light may occur, and the usual precautions must be taken to ensure high insulation and a constant source of potential.

The author desires to thank Mr M. G. Bennett, M.Sc., for the loan of opal glass bulbs.

* T. H. Harrison, *loc. cit.*

THE NEON DISCHARGE TUBE PHOTOMETER

By J. H. J. POOLE, Sc.D., and H. H. POOLE, Sc.D.

MS. received April 12, 1930. *Read June* 5, 1930.

ABSTRACT. A description is given of a form of photometer which uses the rate of flashing of a neon discharge tube, when shunted by a suitable capacity, to measure the current from a photo-electric cell. The general design and standardisation of the instrument are discussed, and curves illustrating its behaviour are given. Finally some practical trials with it for sub-aqueous light measurements are described.

§ 1. INTRODUCTION

THIS photometer is based on the fact that, if a neon discharge tube is shunted by a suitable condenser and connected in series with a high tension battery and a high resistance, the discharge through the tube is not continuous, but consists of a series of uniformly timed flashes. This phenomenon was discovered in 1922 by Messrs Pearson and Anson*, who further showed that the period of the flashes was approximately proportional to the product of the resistance and the capacity for any given tube and voltage. Since that date a large quantity of work has been carried out on this and similar phenomena, and it has been shown by W. Clarkson and others that the time of flash T is given by the relation $T = K(V_m - V_n)/C$, where C is the charging current, V_m the potential at which the discharge starts, V_n the potential at which it stops, and K the shunting capacity. For a given tube V_m and V_n are very nearly constant and independent of C. This equation, however, only holds as long as the duration of a single flash is small compared with the interval between successive flashes.

§ 2. APPLICATION OF NEON TUBE TO PHOTOMETRY

This relation thus gives us a very simple method of photo-electric photometry. It is only necessary to substitute a photo-electric cell for the usual high resistance, and the rate of flashing of the tube will evidently be some function of the illumination falling on the cell. The form of this function will depend on the characteristics of both cell and tube. As the voltage drop across the cell is not constant, it is best to employ a vacuum photo-electric cell, for which the sensitivity does not change very rapidly with change of voltage. In this case we would expect that the rate of flashing should be very nearly proportional to the illumination, and this is borne out in practice. Furthermore, the photometer can easily be arranged to measure very different illuminations by varying the size of the shunting capacity, a feature which is of importance in daylight photometry, where the changes of intensity are

* S. O. Pearson and H. St G. Anson, *Proc. Phys. Soc.* **34**, 204 (1922).

so large. It is to be observed that the method really measures the time integral of the illumination during the period of observation, a fact which may be of advantage in certain cases.

For the first practical tests carried out with this form of photometer, the reader may be referred to a paper published in the *Scientific Proceedings of the Royal Dublin Society**. In this series of experiments an ordinary type of commercial neon lamp was employed. This lamp functioned not too badly, as the curves published in that paper indicate, but since that date certain alterations have been introduced by using a special type of neon discharge tube kindly manufactured for us by the G.E.C. Research Laboratories, Wembley.

There is a danger with the original simple arrangement of circuits that small leakage currents may pass through the condenser or the glass of the neon lamp, or that, under adverse atmospheric conditions, more serious surface leaks may occur. The result is that a certain illumination of the photo-electric cell must be reached before any flashes occur in the lamp, and for greater illuminations the rate of flashing is proportional to the excess above this threshold value, and not to the total illumination. The curves given in the original paper show that this effect is unimportant in the dry air of a heated laboratory, but it was soon found that when used out of doors appreciable errors might occur.

The obvious remedy for such surface leaks was accordingly adopted. Metal strips kept at a suitable potential were partially embedded in the sealing wax which forms the surface of the condenser so as to form guard-rings surrounding the terminals. The special neon discharge tube, previously mentioned, was substituted for the standard neon letter lamp. This tube has a spherical bulb about 5 cm. in diameter, with electrodes of stout wire entering at opposite poles. The electrodes are completely sheathed in glass except for a few millimetres at their ends, and the spark gap between their ends is about 2 to 3 mm. This type of construction allows a tin-foil guard-ring to be gummed round each electrode. Moreover, the luminous flashes, being confined to the small exposed tip of the cathode, are always in the focus of the eyepiece and hence are very readily visible.

The behaviour of the tube was found, however, to depend on the potential of the glass of the bulb, which, in turn, depended on the dryness of its surface. Thus, under certain conditions, the tube was liable to give a faint continuous discharge, while, under others, an occasional flash would be of quite a different nature from the others, being blue instead of red, and much more intense. The interval after one of these bright flashes was always longer than the normal, showing that a greater fall in potential had occurred. To remedy these defects various expedients, such as coating the surface of the bulb with tin-foil maintained at some definite potential, were tried. The best results were obtained by completely enclosing the bulb in a block of paraffin wax, leaving only a small window to observe the flashes, and fitting guard-rings, both on the glass and on the surface of the wax block, round the negative terminal.

* J. H. J. Poole, *Scient. Proc. Roy. Dublin Soc.* **19** (N.S.), No. 3, 17 (1928).

§3. ELECTRICAL CONNEXIONS OF PHOTOMETER

The general lay-out of the electrical connexions is shown in Fig. 1. The wooden box containing the condensers A, B, C, D, the neon tube N, and the safety resistance R (about 20,000 ohms) is indicated in section. Its shape has been modified to show the electrical connexions more clearly. The guard-ring surfaces are all connected as shown to the terminal G, the positive terminal being insulated with paraffin wax from its surrounding guard-ring, which is itself mounted on an ebonite plate. The negative terminal passes through a paraffin wax bush in this plate. The photo-electric cell P is inserted between the positive of the battery and the positive terminal.

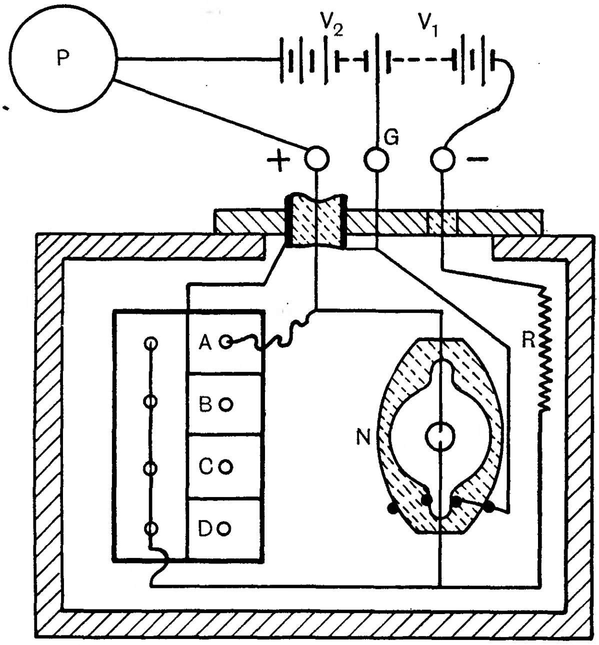


Fig. 1.

It is evident that, if V_1, the potential of the guard-rings, is greater than the flashing potential of the lamp, surface leaks would cause flashes even with no current through P. This "dark current" can easily be measured and allowed for, if it is small and tolerably steady. On the other hand, if V_1 is too small, surface leaks would prevent any flashes until a certain "threshold" illumination is reached, as already explained. It is advisable to adjust the value of V_1 so as to give a very small dark current, which can then easily be allowed for.

The potential across the photo-electric cell varies, throughout the cycle of changes in the neon tube potential, by some 10 to 20 volts, depending on the particular neon tube used. The mean potential across the terminals of the tube, for any complete number of cycles, is, however, nearly constant. If we call this mean potential V and the excess of total battery potential over the guard-ring potential V_2, the effective potential across the photo-electric cell is $V_1 + V_2 - V$. This must be

high enough to ensure that small changes in its value have only a very slight effect on the sensitivity of the cell. For further information on this point the reader may consult the previous paper*.

The capacities of the four condensers A, B, C, and D are approximately 0·5, 0·05, 0·005, and 0·0005 μF respectively. If there were no outside capacities in parallel with these, the corresponding sensitivities would be in the ratios 1 : 10 : 100 : 1000, but it must be remembered that the capacity of P and the pair of cables leading to it must be added in order to obtain the effective capacities which control the ratios on the different ranges. These external capacities are negligible in comparison with 0·5 μF, so that the current sensitivity of the apparatus when used on condenser A is independent of the particular photometer and leads to which it is connected. With the smaller condensers the effect becomes increasingly important, so that the factors for converting the readings on the more sensitive ranges B, C, and D to the standard range A must be found for each particular set of circumstances.

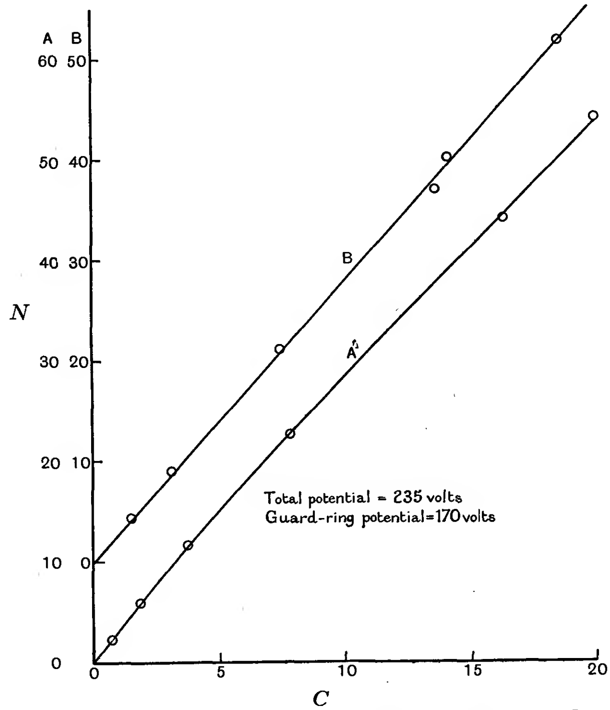
This external capacity is especially important in the case of a submarine photometer with long cables. If the surface of the rubber insulation is perfectly dry the effective capacity even of a pair of 100-yard cables is not very great, especially if they are separated from each other. When, however, they are immersed in the sea, their capacity is much increased. Fortunately, under these circumstances it has a definite value, which is not appreciably changed by hauling in the cables and coiling them down together in a box, as the film of salt water on the surface of the cables acts as a conducting sheath. Accordingly, for submarine work, the cables should be kept wet, so as to keep their capacity constant. This capacity effect greatly reduces the sensitivity of the apparatus for relatively deep water work. Thus the mutual capacity of a pair of 100-yard cables was estimated to be about 0·0045 μF, while the value found for the cables coiled in a box and partly wet with fresh water was 0·0033. An external capacity of 0·0045 μF would reduce the factor for the D range from 1000 to 100.

§4. STANDARDISATION OF PHOTOMETER

To standardise the photometer a 10^5 ohm resistance was connected in the circuit between the photo-electric cell and the positive terminal of the neon tube, so that the current could be directly measured with a potentiometer. By using different cells and illuminations ranging from that of a small gas-filled lamp up to bright sunlight, a long series of current values was obtained. The results are given below for the various condensers. For the smaller condensers B, C, and D a cell with short, low-capacity leads was used. With condenser A the capacity of the leads of the submarine cell used for some of the readings is negligible. The guard-ring potential used gave no appreciable dark current.

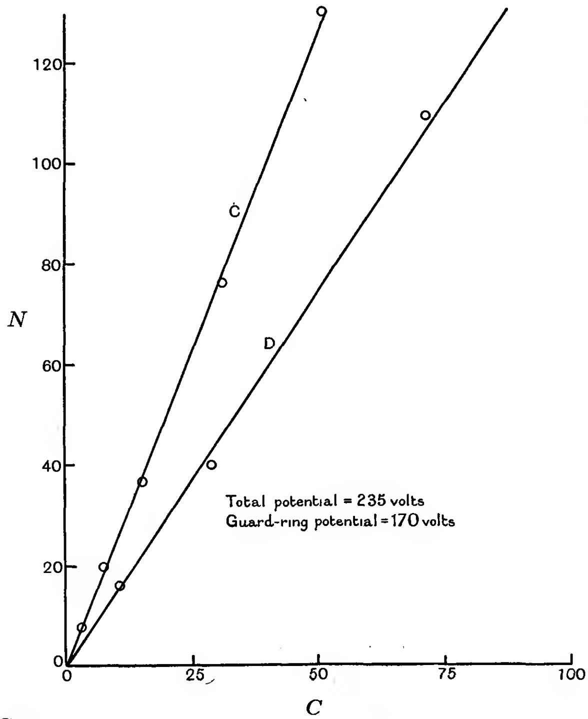
We have plotted in the graphs shown in Figs. 2 and 3 the current C against the number N of flashes per minute. Each curve is labelled with a letter corresponding to the capacity used. The value of N can be read directly off the graph while the value of the current scale appropriate to each condenser is given in the legend. It

* J. H. J. Poole, *loc. cit.*



Curve A: 1 *unit* = 10^{-6} *amp.* *Curve B:* 1 *unit* = 10^{-7} *amp*

Fig. 2.



Curve C: 1 *unit* = 10^{-8} *amp.* *Curve D:* 1 *unit* = 10^{-9} *amp.*

Fig. 3.

will be seen that the curves for the smaller three condensers are practically linear, but for condenser A there is a distinct curvature. Higher rates of flashing than those shown in the curves were also tried, but were found not to give satisfactory results. The limit of accuracy obtainable is probably not greater than 5 per cent. As a matter of fact it was found that, apart from surface leaks, the commercial type of neon lamp was in some respects preferable. Some tests with it, using a diode as a current limiter, gave a linear relation for all four condensers, and the variations from the mean value of C/N were less. The flashes for the lower pair of condensers were, however, very feeble and difficult to observe, and in this respect the new form of tube is certainly better. The bright blue flash was never observed in the commercial letter type of lamp, which is a point in its favour. From these considerations it is plain that the best type of discharge tube has not yet been obtained. It is intended to conduct further trials on a tube with point and plate electrodes, in which it is hoped that the plate electrode will tend to make the discharge more regular by screening off any electrostatic effect due to charges on the glass walls of the tube.

§ 5. APPLICATION OF PHOTOMETER

As an example of the use of the photometer in the field, some measurements on the penetration of light into the water of Lough Bray, Co. Wicklow, may be briefly cited. This lake is at an altitude of about 1000 ft. above sea level and is overhung on the west and northwest by a steep hillside. The water is generally at about pH 4·8 and is deeply stained with peat. Phytoplankton is almost entirely absent. Measurements were made from a small boat, moored in a part of the lake where the depth was about 40 metres.

A photometer containing a Burt vacuum sodium cell and specially designed for marine measurements was used under water, while the aerial illumination was found from the simultaneous readings of another photometer, which contained a vacuum sodium cell made by the General Electric Company. Both photometers were fitted with opal windows. Unfortunately, the submarine photometer proved to be somewhat unsuitable for work in the lake, as the capacity of the long cables fitted to it greatly detracted from the sensitivity of the apparatus. These cables are about 90 metres long, which is necessary for work at sea but quite useless in Lough Bray where the water proved to be so opaque to blue light that the illumination at a depth of 4 metres could not be measured.

A two-way switch was connected in each photometer circuit in such a way that the photometer current could be passed through the neon lamp or diverted to the guard-ring at will. Thus, by moving the two switches, either photometer could be brought into use while the one not in use was still subjected to a voltage not very different from the average when connected to the lamp. This precaution has been found necessary in marine work to prevent small soakage currents through the cable insulation which were noticeable for a short time after applying a potential difference to them.

The measurements were made on August 26, 1929, between the hours of 2·30 and 4 p.m. G.M.T. There was bright sun and a strong westerly wind. The extraordinary opacity of the water rendered the measurements somewhat difficult, as

small variations in depth caused such rapid changes of illumination. Moreover, owing to our inexperience of the method, the best order of observations was not adopted, so that the results can only be regarded as approximate. Nevertheless, the experience gained showed that the apparatus could be used in reasonably smooth water even in a small rowing boat.

The results are summarised in Table 1, which shows the ratio of the number of flashes per minute for the immersed photometer with the condenser given in the first line to the number of flashes per minute for the air photometer, which in all cases was used with condenser A.

Table 1: Ratio of numbers of flashes per minute for the immersed photometer with condensers A, B, C, D, and the air photometer

Depth in metres	A	B	C	D
In air	4·60	—	—	—
1	—	0·236	—	—
2	—	—	0·111	—
3	—	—	—	0·103
4	—	—	—	0
3	—	—	—	0·013
2	—	—	—	0·156
1	—	0·192	1·25	2·67
In air	4·80	—	—	—

A small dark current through the immersed photometer causing two flashes per minute with condenser D was corrected for in determining these ratios. The readings with the condensers B, C, and D at 1 metre give the relative sensitivities for the three with the cables in use, while other tests have shown that the sensitivity with condenser B is about nine times as great as with A, this ratio being only slightly affected by the capacity of the cables. Bringing in the appropriate factors for the condensers, and taking means for the descending and ascending readings, we get the values shown in Table 2 for the percentage illumination P at different depths and the mean vertical absorption coefficient μ for each successive metre. The value of μ for the first metre is based on the assumption that 85 per cent. of the light is transmitted by the surface.

Table 2: Percentage illumination P at different depths and mean vertical absorption coefficient μ for each successive metre

Depth in metres	P per cent.	μ
0	100	5·1
1	0·5	2·6
2	0·035	1·25
3	0·01	—
4	0·00	

The enormous value of μ for the first metre—about fifty times that for sea water—is almost certainly due to the deep brown colour of the water, which very rapidly

absorbs the blue, violet, and ultra-violet rays to which the cell is sensitive. The longer waves near the limit of sensitivity of the cell, which is in the neighbourhood of 5000 A.U., penetrate rather deeper, so that μ decreases with increase of depth. The white window of the photometer was just visible at a depth of about 1·75 metres. In clear sea water it would probably be visible down to at least 10 metres, but the relative opacity of the water compared with sea water is evidently not nearly so great when judged visually as the value found by the blue-sensitive cell.

§ 6. CONCLUSION

The preceding results plainly show that this form of photometer cannot be used for highly accurate photometric work. It is, however, eminently suitable for daylight photometry in which the natural fluctuation of the light renders extreme accuracy impossible in any case. Furthermore, it can be employed in situations which, due either to motion or vibration, render the use of a galvanometer or electrometer impossible. It is only in such situations that we would use the instrument, as, of course, a galvanometer is a much more convenient instrument to employ if it can be set up. The discharge tube photometer, however, possesses advantages on the score of immunity to shock, and rapidity of assembly, which may in certain cases outweigh the ease of galvanometric reading. It is essentially a field and not a laboratory instrument.

In connexion with the work at Lough Bray we should like to thank the Hon. A. E. Guinness for permission to make the measurements and for the use of his boat for the purpose.

THE PHOTO-ELECTRIC CELL AS AN ESSENTIAL PART OF THE RECORDING MICRO-PHOTOMETER

By PETER PAUL KOCH, Hamburg.

MS. received April 16, 1930. *Read June* 5, 1930.

ABSTRACT. Reference is made to the methods of photographic photometry, and the characteristics of the photo-electric cell which are of importance in its application as a light-sensitive detector to the measurement of photographic densities are described. It is shown that, with proper manipulation of the cell, the effects of lag, fatigue, and recuperation may in practice be ignored. Finally, reference is made to the special advantages of the compensation method, which makes the results obtained with the registering photometer independent of the intensity of the source used for illuminating the photo-electric cell.

THERE are many well-known reasons why the methods of photographic photometry, which originally attracted scarcely any attention, have in recent years developed until they rank among the more important methods of measurement in modern physics. There is no doubt that, because of the various incompletely investigated peculiarities of the photographic plate, its use in photometric investigations involves a certain amount of indirectness. It is certainly desirable that the different problems which at the present time must be solved by means of photographic photometry should be investigated by direct measurement with energy-sensitive devices, but for these purposes their present sensitivity should be increased by several powers of ten. Granted the impossibility of avoiding the photographic plate, the best way to use it consists in calibrating it by means of marks made by lights of known intensities. In this connexion many simple and suitable methods have been described which render harmless the disadvantages of the photographic plate.

The calibration of plates so prepared requires the measurement of opacities and that in turn is a photometric problem. Because of the enormous mass of photometric results which can be obtained from the records made on a single photographic plate the use of the eye as a photometric organ soon proved to be too slow. For that reason, even in the first recording photometer constructed, the eye was replaced with the greatest success by a photo-electric cell*.

In 1911 Elster and Geitel† published very detailed directions for constructing photo-electric cells. If these are followed no one will have difficulty in manufacturing the cells for himself. At the present time the filling of the cells with inert gases has been made simpler by the possibility of procuring these gases cheaply in any quantity.

* P. P. Koch, *Ann. d. Phys.* **39**, 705 (1912).

† J. Elster and H. Geitel, *Phys. Z.* **12**, 609 (1911).

In the photo-electric cells of the type introduced by Elster and Geitel the change of current follows that of the illumination with such great rapidity that the cells have proved to be eminently suitable for the technical problems of photo-telegraphy, television, and sound films. The recording photometer, however, makes essentially greater demands upon the cell, and thus the cells first used with this instrument showed too much inertia*. The reason was that in these cells only one hemisphere was coated with the silver and photo-electric metal, such as potassium, the other hemisphere being left free for the admission of light. This half, as a result of the method of construction, is now necessarily coated with a very thin though practically transparent film of potassium. If the illumination changes, the film is charged to varying potentials and, owing to its great resistance, the charges can leak away but slowly. In the meantime they exert an electrostatic influence on the anode of the cell, which is connected to the recording electrometer. It was possible to eliminate this trouble completely by covering the entire surface of the cell with potassium except for a small opening to admit light.

This type of photo-electric cell, which has been used for fifteen years as a light-sensitive organ in the recording micro-photometer, has always behaved exceedingly well. Its freedom from inertia is so complete that there are practically no restrictions on the speed of recording with the micro-photometer, and the measurements, within the most advantageous range, may always be repeated with a photometric precision of 1 per cent. It is necessary to ensure that the voltage applied to the cell is not too close to that which causes a glow discharge, otherwise there will be serious troubles which are characterised as phenomena of fatigue and recovery. Rosenberg† has made a detailed investigation of these phenomena and has fully described them. He attributes them to the covering of the light-sensitive alkali metal by gaseous ions. The covering layer of gas varies with the experimental conditions. Whatever the cause, there is no doubt that the trouble may be completely eliminated by keeping the voltage applied to the cell about 10 per cent. below that of the glow discharge‡. The sensitivity of the cell is then still quite sufficient for use in the recording micro-photometer.

The photo-electric cell is superior to all other light-sensitive organs now at our disposal in one important respect, namely, that a method of compensation can be used § so that the indications of the recording photometer are independent of the candle-power of the light source used to illuminate the photo-electric cells. In consequence there is no need to take precautions to keep the light source constant by controlling the current or voltage supplied to the lamp. It is quite sufficient to connect the lamp to any circuit, the voltage of which may vary within considerable limits.

There is no doubt that a retrograde step has been taken in the many recent designs which abandon the method of compensating the variations in intensity of the light source. It is useless to obtain, instead of the compensation, a close proportionality between the deflection of the measuring instrument and the intensity

* P. P. Koch, *loc. cit.* p. 724.

† H. Rosenberg, *Z. f. Phys.* **7**, 18 (1921).

‡ P. P. Koch, *Z. f. Instrk.* **45**, 494 (1925).

§ P. P. Koch, *Ann. d. Phys.* **39**, 708, 733 (1912).

of the light admitted to the cell, since careful calibration is required in order to establish the fact that such proportionality really exists. It is only a question of aesthetic interest whether the calibration curve thus obtained is a straight line or not. Since, moreover, as explained above, in investigations involving photographic photometry the photographic plate must always be provided with marks of known intensity, the connexion between the intensity of light falling on the cell and the deflection of the measuring instrument is completely eliminated from the required result, for example, the *intensity distribution* in a spectral line. In consequence the connexion is a fortiori of no account!

SOME FACTORS AFFECTING THE SPEED OF THE KOCH MICRO-PHOTOMETER

By E. A. BAKER, D.Sc., F.R.S.E.

MS. received April 17, 1930. *Read June* 5, 1930.

ABSTRACT. The time taken by a photo-electric photometer of the Koch type to arrive within 1 per cent. of its equilibrium value is examined and an account given of the methods adopted to reduce this time in a practical case. The best results were obtained by using a "leak" cell with a small central cathode and by avoiding large windows or other insulating surfaces in the cells. In these ways the response time is readily reduced to half a second, but is not brought below a tenth of a second even with very high illuminations on the cells.

IN the simplest form of photo-electric micro-photometer a beam of light passing through a photographic plate falls on a photo-electric cell which has its cathode at high negative potential and its anode connected to the thread of a "string" electrometer, and also through a high resistance leak to earth.

Regard the cell for the moment as a high resistance inversely proportional to its illumination. Denote its resistance by X, that of the leak by Y; denote the voltage on the cell cathode by V and that on the electrometer thread by v; and denote the capacity of the electrometer thread and its connexions by C. The rate of change dv/dt of the electrometer voltage is then given by

$$C.dv/dt = V/X - v\,(1/X + 1/Y),$$

so that
$$v = YV/(X + Y) + K\,.\,\exp\,[-\,t\,(X + Y)/CXY],$$

where K is a constant depending on the initial conditions. From this equation Koch* finds that the time required for the thread to arrive within 1 per cent. of its equilibrium value $YV/(X + Y)$ after a change in the cell resistance from infinity (cell in darkness) to X, is given by

$$T = 4{\cdot}7\;CXY/(X + Y),$$

T being in seconds and C, X, Y in electrostatic units. Inserting the equilibrium value of v, we have

$$T = 4{\cdot}7\;CXv/V.$$

If the period of the electrometer is short compared with T, the value of v may be taken without error from the position of its index.

In the photo-electric cell the relation between current and applied voltage is of course not one of direct proportionality; nevertheless, the deviations are not by themselves sufficient to invalidate the general conclusion that T may be diminished without limit by raising V and by lowering v, C, and X, the last by increasing either the sensitiveness of the active deposit in the cell or the intensity of the light.

* P. P. Koch, *Ann. d. Phys.* **39**, 705 (1912); H. Beutler, *Z. f. Instrk.* **47**, 61 (1927).

In the Koch photometer the leak is replaced by a second photo-electric cell, called the "compensating" or "leak" cell to distinguish it from the other or "main" cell. Some years ago a photometer of this type was made and set up at the Royal Observatory, Edinburgh, for use on stellar spectra. The instrument will, it is hoped, be fully described in the complete account of the work for which it was designed, and of which preliminary results have already been published*. One of the chief difficulties was to reduce the value of T sufficiently, for the spectra are numerous (several hundreds being taken each winter) and each is some 30 mm. long, while the rapid changes of contrast, especially in the case of spectra showing bright lines, make it essential not to work at a greater speed than about 0·025 mm. in T seconds, corresponding to 20 T minutes per spectrum recorded. Indeed, the work could scarcely have been performed with an instrument so slow as the original Koch photometer or any of the earlier thermo-electric micro-photometers.

The effects of raising V, the high potential on the main cell, are well known. If the sparking potential is approached too closely (the limit depending on the intensity of the light) a drift occurs, and to keep this drift within the desired limit of say 3 per cent. per hour it has been found inadvisable to use a helium-filled cell at over 120 volts, or an argon-filled cell at over 160 volts.

The sensitiveness of the electrometer, which fixes the value of v, may in some cases be limited by the amount it is desired to spend on its plate batteries. If, for example, the instrument is working at a sensitiveness of 100 mm./volt, it follows that a change of 1/100 of a volt in the potential of either plate battery will cause a shift of 1 mm. in the zero of the instrument. This difficulty can be avoided by charging the thread to a high potential and connecting one plate to the cells; but this increases the value of C. In addition, the period of the thread must be kept short, so that sensitiveness must be gained by increasing the magnification rather than by slackening the thread. In the Edinburgh electrometer the thread is held between inelastic supports, and, the temperature compensation being imperfect, it has been found advantageous to use a fairly thick thread and to depend on its elasticity rather than on its tension for control. A sensitiveness of 100 mm./volt can be attained over the full scale, but only one-quarter of this is actually employed.

In Koch's original instrument† the value of C was 35 cm., and in Goos's‡ as high as 60 cm. In the Edinburgh instrument it was found possible, by connecting the internal electrode of the "leak" cell in place of its wall to the electrometer thread, to reduce this capacity to 15 cm. Further appreciable reduction would mean reconstructing the thread supports of the electrometer.

Cells of sensitised potassium are used. The area of photographic plate through which the light beam has to pass is fixed by the resolving power required, and, since the plates are not perfectly flat, large aperture ratios in the incident and emergent beams cannot be used; but the intrinsic brightness of the source can be greatly augmented by overrunning it. Were the cost of replacement of the lamp the sole consideration it should obviously be run at such a current as will give the maximum

* R. A. Sampson, *Monthly Notices R.A.S.* **83**, 174 (1923); **85**, 212 (1925).

† P. P. Koch, *loc. cit.*

‡ F. Goos, *Z. f. Instrk.* **41**, 313 (1921).

number of records per lamp. Actually, lamps of the gas-filled motor headlamp type are so cheap that the cost of replacement is inconsiderable until the life has been reduced to a few hours. A life of from 50 to 100 hours is ample.

According to the theory given, the increase in X which may be obtained in this way should suffice to reduce T to the order of a tenth of a second or less. That such a reduction is not attained in practice is due to the defects of the photo-electric cell. In cells of the type shown in Fig. 1 (*a*) the design is at fault. The large areas of insulating surfaces in the cell, coupled with the inefficient ring anode, make this type of cell useless for rapid work. In the Edinburgh instrument the design of cell used (Fig. 1 (*b*)) is due to R. T. Beatty*. Response curves obtained by using cells of

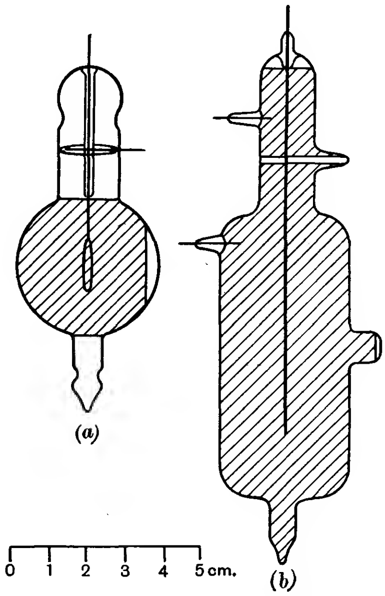


Fig. 1. Forms of photo-electric cells. (*a*) Faulty type. (*b*) Type employed. Shaded parts are silvered.

these types as main cells are shown in Fig. 2, for values of the light intensity increasing by powers of ten. These curves show the recovery of the photometer index to the 100 per cent. value after occulting the beam on the main cell for 30 seconds: if instead a period of occultation of only half a second is used, the two types of cell shown in Fig. 1 (*a*) and (*b*) both give results almost identical with the full curves of Fig. 2, except in the final case corresponding to the brightest illumination, where the shorter time of occultation gives a smaller overshooting of the equilibrium value.

From these curves it appears that the value of T, the time for response within 1 per cent., is actually increased instead of diminished by the final increase in the illumination. This effect is due, not to the main cell, but to the "leak" cell, for if this cell is replaced by an ohmic leak the effect disappears. In all the cases shown in Fig. 2 the leak cell resembled that shown in Fig. 1 (*b*), except that the sensitive surface was on a small metal plate fixed to the internal electrode.

* R. T. Beatty, *Phil. Mag.* 33, 49 (1917).

If the behaviour of this leak cell is typical, it would appear that T cannot be reduced much below a tenth of a second with the Koch arrangement, and that for periods below this an ohmic leak must be used; but it is seldom that illuminations of the order of those of Fig. 2 (*d*) are permitted by considerations of resolving power, and in normal cases, corresponding to Fig. 2 (*b*), it seems probable that the use of a leak cell with a tendency to cause overshooting (due of course to an increase in the sensitiveness of this cell following a light current) is of assistance in shortening the period.

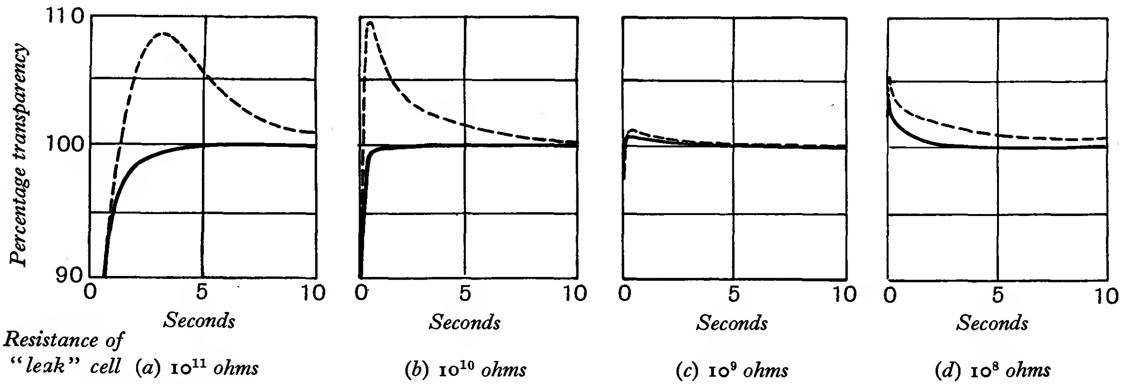


Fig. 2. Changes in recovery curves with increasing illumination, after occulting light on main cell for 30 seconds. Dotted curves—main cell as in Fig. 1 (*a*). Full curves—main cell as in Fig. 1 (*b*).

One other effect of using a leak cell with internal cathode may be mentioned, since it renders more valid a criticism already brought against the Koch photometer*. This is that the deflections are far from being proportional to the transparency of the negative, making the calibration of the scale dependent on the sensitiveness of the electrometer. This inconvenience can be overcome in one of two ways. Using a main cell well below its sparking potential and an electrometer giving deflections proportional to the voltage of its thread, the scale of the instrument depends on the relation between current and voltage for the leak cell. For very small voltages on the cell this relation is approximately linear, and Beutler† recommends the use of this region, in spite of the necessity for a highly sensitive electrometer, giving well over 100 divisions per volt. The writer finds it preferable to avoid the small voltages altogether‡, and to use the leak cell over a range of voltage of say from 3 to 8 volts, where, by suitably adjusting the pressure of gas in the cell, its current-voltage relation may be made strictly linear.

* G. Hansen, *Z. f. Instrk.* **47**, 71 (1927).
† H. Beutler, *loc. cit.*
‡ Cf. E. A. Baker, *Journ. Scient. Instr.* **1**, 345 (1923–4).

THE USE OF THE PHOTO-ELECTRIC CELL IN SPECTROPHOTOMETRY*

By Dr K. S. GIBSON,

Physicist, Colorimetry Section, Bureau of Standards.

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ABSTRACT. The greatly increased use of colour in industry and the home makes it highly important that methods for the rapid and accurate analysis and specification of colours be available. The only complete method of analysis of colour stimuli and the most fundamental method of specification is the spectrophotometric method. Of the various methods of spectrophotometry available, that using the photo-electric cell can be made by far the most rapid and probably has the highest precision of any available. The advantages and limitations of the new photo-electric spectrophotometers are discussed, particularly the bearing of various factors on the accuracy of the results obtained by them. Previous uses of the photo-electric cell in spectrophotometry are briefly described.

§ 1. INTRODUCTION

THERE has been in recent years a great increase in the display and use of colour, both in industry and the home. From automobiles to cooking-utensils and from coloured cinematograph pictures to coloured bath-tubs, the eye is continually impressed with a profusion and brilliance of hues in striking contrast with the unsaturated colours of a generation ago. Hardly is there an article of commerce in which colour is not inherently connected with the quality of the product or in which colour is not used directly as an aid to salesmanship.

This widespread use and admitted importance of colour has been accompanied by an increasing demand for more reliable means of specifying colours. Almost invariably in the manufacture and testing of coloured materials there comes a time when it is desired to maintain and control the primary or working standards of colour to a precision hitherto considered unnecessary or impossible and to differentiate to a finer and more certain degree between colours almost alike. In many cases such standardisation and discrimination have been attempted in terms of certain colour systems or by means of certain colorimeters. However useful such methods may be in various special cases, the realisation gradually comes to most investigators, as has long been known to experts in the field, that precise and fundamental specification is usually impossible by such means. They come to realise that it may be unsafe to trust to the permanency or reproducibility of material colour "standards," that in general no two observers will get identical results when matching the colours of energy distributions that are dissimilar, and finally that colorimetric methods, in general, furnish them little analysis of the stimulus evoking the colour.

* Publication approved by the Director, Bureau of Standards.

Such an analysis can adequately be made only by spectrophotometric methods. Furthermore, such spectrophotometric data furnish, *per se*, the most fundamental specification of the colour stimulus which it is possible to obtain. Such a specification is unique and unambiguous and is independent of variations or differences in the observers' colour vision (or of variations or differences in the spectral sensitivities of whatever detectors are used). If, as is often the case, it is desired to express the spectrophotometric data in colorimetric terms, this may be done by computing the trilinear coordinates (or the dominant wave-length and colorimetric purity) and the transmission or reflectance for the specified illumination. For this purpose* it is necessary to know or assume, in addition to the spectral transmission or spectral reflectance of the sample, the relative energy distribution of the light-source by which the sample is to be viewed, the relative energy distribution that is to occupy the centre of the Maxwell triangle, and the "excitation" and "visibility" data to be taken as representing the normal average eye. While this may seem somewhat complicated, the end result is a specification of colour based upon fundamental data, independent of material colour "standards," and referred to a hypothetical average normal eye.

In addition to the importance of spectrophotometric measurements in the specification of colours, there is the other broad field of application, not only in the visible part of the spectrum, but also in the ultra-violet and infra-red, where the spectrophotometric analysis is itself the desired goal. This is true, for example, in investigations of the chemical structure of organic and inorganic compounds, in the study of dyes and dyed fabrics, in the testing of eye-protective glasses, and so on.

The fundamental importance of spectrophotometric measurements is well known to all who have given careful thought and study to these phases of optical research. It has, in fact, been well known for a great many years, as is attested by the great variety of spectrophotometric instruments and methods that have been developed and used for this kind of work†. Spectrophotometric measurements have been made visually for over fifty years, and the visual methods have been supplemented in the ultra-violet by photographic methods and in the infra-red by radiometric methods. As apparatus and technique have been improved, the spectral range covered by visual methods has been gradually extended, photographic methods have been applied throughout the visible and into the infra-red

* Methods of making the kind of computations here referred to are considered in the following publications: "Report of the colorimetry committee, Optical Society of America" (L. T. Troland, Chairman), *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **6**, 527–96 (1922); J. Guild, "A critical survey of modern developments in the theory and technique of colorimetry and allied sciences," *Proc. Opt. Convention*, **1**, 61 (1926); D. B. Judd, "Reduction of data on mixture of color stimuli," *Bur. Stand. Res. Paper* No. 163 (April, 1930). All these papers include extensive references to other publications on the same or related subjects. The last one in particular, on pp. 518 and 536, refers to papers by Ives, Guild, Dziobek, Runge, Priest, and Judd of importance in this connexion. Visibility data as recommended by Gibson and Tyndall (*Bur. Stand. Scient. Paper* No. 475 (1923)) were adopted at the sixth meeting of the International Commission on Illumination at Geneva, 1924 (see *Proceedings*, pp. 67 and 232).

† Note, for example, the various instruments and methods described or listed in the report of the committee on spectrophotometry, Optical Society of America (K. S. Gibson, Chairman), *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **10**, 169–241 (1925).

as far as photographic emulsions could be sensitised, and radiometric methods have been likewise extended throughout the visible and into the ultra-violet wherever sources of sufficient intensity in this region were available. In recent years the photo-electric cell has been applied to spectrophotometric measurements, at first in the ultra-violet and shorter wave-lengths of the visible spectrum, and then, with the advent of the new types of cells, throughout the visible and into the infra-red. Combined with vacuum-tube methods of amplification, the photo-electric method gives promise of becoming the most valuable of all spectrophotometric methods, because of the great increase of speed thus made possible. If accuracy is not lost as speed is obtained, reliable spectrophotometric measurement will be greatly facilitated.

§ 2. AMPLIFIED-PHOTO-ELECTRIC SPECTROPHOTOMETRY

As just noted, the modern photo-electric cells, sensitive throughout and beyond the whole visible spectrum, combined with the enormous amplification of current possible with modern vacuum tubes, have placed at the disposal of those interested in spectrophotometry a tool of the utmost importance. The greatly increased speed of determination that has been made possible is alone worth all the effort and expense that may be put on the development of amplified-photo-electric spectrophotometers. The possibilities in this new development are so great that it seems important to consider carefully what the real advantages of the new instruments may be, as well as what their limitations actually and of necessity are.

(*a*) *Advantages of the new photo-electric spectrophotometers*

The principal gain over previous spectrophotometric methods has already been noted—viz., the increased speed of determination that has been made possible. The time required for making spectral transmissive and reflective measurements can apparently be reduced to one-tenth or one-hundredth of that possible with other methods. In view of the rapidly increasing demands for spectrophotometric analysis and colorimetric specification, this is a factor of the greatest importance.

The amplified photo-electric current, which makes possible automatic or semi-automatic operation or the use of rapidly operated galvanometers, contributes directly to this increased speed of determination. These features doubtless also should effect considerable saving of nervous energy and eye-strain, assist in avoidance of blunders, and result in increased precision. Whether a self-recording instrument is desired depends, of course, on the use to which the results are to be put. For computation, values are desired; and, if the instrument gives curves, values must be read from them before the computations can be carried out. For illustration, on the other hand, curves are desired; and, if the instrument gives values, they must be plotted and the curves drawn.

In addition to speed and the possibility of automatic operation, there is one other way in which the photo-electric method is apparently superior to others—viz., as regards precision. *This should not be confused with accuracy*, which is considered later. By precision of measurement is meant solely the reproducibility, regardless of whether the values obtained are correct or incorrect. A precision of the order

of magnitude of 0·1 per cent. has been claimed in several cases for photo-electric spectrophotometers, both with and without amplification. This claim is perhaps not unduly optimistic, although it remains to be demonstrated, at least with the modern commercial instruments, whether such reproducibility can be maintained in practice, not merely in two consecutive runs, but from day to day and from month to month. Undoubtedly the photo-electric cell is superior to the eye (with which it is usually compared) in this respect, especially if one considers the greatly differing speed of determination and the difficulty which the eye has in the end regions of the visible spectrum. However, it is quite the custom to consider the eye as being much poorer than it really is. Lack of precision in visual spectrophotometry (except, of course, in the end spectral regions) is in most cases probably a result of carelessness, poor technique, or poor photometric field. An experienced observer with a good instrument can, by averaging five or ten observations at each wave-length, readily obtain a mean whose probable error is but a fraction of one per cent.; and, in general, the gain in precision which the photo-electric cell makes possible, *other things being equal,* would not be of particularly great importance were it not combined with such a notable increase in speed.

Speed of determination is the outstanding feature of importance in the amplified-photo-electric spectrophotometers.

(*b*) *Limitations of the new photo-electric spectrophotometers*

If one were to believe some of the statements appearing in newspapers and journals concerning the new spectrophotometers, even the statements appearing in some of the technical articles describing the instruments, one could well assume that a cure-all had at last been found for all spectrophotometric and colorimetric problems. Some of the statements that have been made in connexion with descriptions of the new instruments are quoted below. These quotations may be divided into two general classes: (*a*) Those which contain distinctly erroneous statements, and (*b*) those which may be essentially true, but are very misleading in the implication that the instrument being described does something that has never been possible before. The class into which the quotation may be put is indicated by the designation, (*a*) or (*b*), as defined just above.

(*a*) "...a complete record of a colored sample can be obtained in less than ten seconds." (The inaccuracy of statement here is in the words "a complete record," as the article is referring particularly to reflection measurements. See further discussion below.)

(*b*) "Whereas previous spectrophotometric methods for use in colorimetry have made use of a standard white as a basis of comparison, the new instruments give an absolute measurement, independent of variations in either the source of light or the photoelectric cell."

(*b*) "This photoelectric method of measuring color may enable the oil chemist to make use of a method of color measurement that will disclose fundamental data."

(*b*) "...it is said to be possible to match a color perfectly without ever seeing the actual color. It has been found possible, by use of the apparatus, to differentiate

between two colored samples known to be of different compositions but which appear exactly alike to the eye."

(*a*) "...by a novel utilization of photoelectric cells we have developed means whereby it is now possible to measure accurately, i.e., within 0·1 %, the quantity of light transmitted by or reflected from a substance for each wave length in the spectrum...even the trained human eye rarely can detect variations in density less than 2·0 %. With these instruments the accuracy of determination of hue, saturation, etc., is many times greater than that obtainable by visual methods of measurement."

(*a*) "The next exhibit...shows the transmission curves of four Lovibond red glasses...these curves are based upon measurements made photo-electrically... our measurements were made with an accuracy within 0·1 %." (One of these particular transmission curves, for which an accuracy of 0·1 per cent. is claimed, is *known* to be in error at certain spectral regions *by over* 20·0 *per cent.*)

(*b*) "It would seem, therefore, that a method of color analysis that develops data expressed in terms of basic physical facts...would be highly desirable, and such a method is now available."

(*a*) "The spectral absorption of any substance is a direct function of its chemical constitution and physical characteristics, but, heretofore, no practicable means has been available to industry for the accurate determination of such fundamental data."

(*a*) and (*b*) "We thus see that this method enables us to determine color characteristics more accurately than the visual method, to discover facts which the visual method does not, and to extend measurements into those spectral regions where the visual method does not apply, and where, at present, the result is largely a matter of guesswork. Thus, with means available for obtaining fundamental data, it now becomes possible to set up standards, mathematically expressed and capable of reproduction, that will enable one to exercise a more rigid control over production and distribution of all sorts of products, and this series of instruments gives to pure and applied research a new set of tools having a degree of accuracy never before attained."

The two points which should be emphasised in this connexion are these:

(1) The kind of results (viz., spectral transmissive or reflective data) obtainable with the amplified-photo-electric spectrophotometers is exactly the same as has been obtainable for many years by other spectrophotometric methods—visual, photographic, thermo-electric, or photo-electric—which have been used to cover the range from the ultra-violet through the visible and into the infra-red. All four methods have been applied in the visible spectrum. What is to be done with the results—whether obtained by the older methods or by the latest methods—is a problem of exactly the same status as before. The spectrophotometer, regardless of kind or make, is merely the tool for the analytical or the colorimetric expert; and the value of the results thus obtainable, their use and application, depend on the knowledge, skill and intelligence of those who are doing the work.

(2) There is no a priori reason why amplified-photo-electric spectrophotometry should be any more accurate than other methods, particularly the visual

method* with which it is customary to compare it. Speed, automatic operation, and reproducibility are no guarantee of accuracy; they may, in fact, have nothing whatever to do with it and may even detract from it. It is ridiculous to make a *general* claim of accuracy to 0·1 per cent. for *any* instrument or method where an incandescent source is used and no slit-width corrections are made to the results.

The new photo-electric spectrophotometers must stand the same tests for accuracy as any instrument. If the results can be proved accurate, well and good; if not, the user must decide how far the advantages listed above make up for questionable accuracy or demonstrated inaccuracy. Not all laboratories require the degree of accuracy desired, for example, at the national standardising laboratories. There are various problems in control work where accuracy may be of secondary importance. This must be decided by the user of the instrument. He should realise, however, that the curve or value obtained may or may not be reliable, even though the instrument will duplicate it any number of times, at a high rate of speed.

The following are the kinds of error to which *all methods* of spectrophotometry are liable, *including the new photo-electric spectrophotometers*:

(1) *Errors in the wave-length calibration.* This is very important. With certain types of transmission or reflection curves (those showing rapid variations with wave-length) an error of even half a millimicron may cause errors of many per cent. in the values obtained.

(2) *Errors resulting from the use of finite slit-widths.* These will be most serious where the spectrophotometric curves show the greatest curvature, being determined mainly by the second derivative of the "luminosity" curves (visual or photo-electric) resulting from (i) the energy distribution of the source, (ii) the dispersion of the prism, (iii) the spectral sensitivity of the receiver, and (iv) the spectral transmission or reflectance of the sample. There are many kinds of work where the error may be negligible; but results obtained with transmission or reflection samples of any considerable selectivity cannot be certified to 0·1 per cent. unless the slit-width corrections are made. Experimentally, such errors may be greatly reduced by the use of narrow slits. The slit-widths which it is safe to use without making corrections to the results depend on the selectivity of the sample and the use to which the results are to be put.

(The two errors noted above may be eliminated at certain wave-lengths by the use of mercury or helium sources, the homogeneous energy from these sources being used to make the measurements.)

(3) *Errors resulting from stray energy.* The radiant energy passing the telescope slit of a spectrophotometer is composed mainly of the narrow range of wave-lengths nominally transmitted for the particular wave-length setting of the instrument, but there is, in addition, a certain amount of energy of all wave-lengths, "stray light," mixed with the approximately homogeneous energy. Throughout the spectral region of greatest sensitivity the effect of the stray energy is usually

* Except perhaps in the end regions of the visible spectrum. It may be noted, however, that the full possibilities of the visual method have been seldom realised in practice.

negligible (although not always so in certain types of very low transmission); but, in those regions where the detector is relatively insensitive, its response to the stray energy may be greater than to the homogeneous energy and large errors may be made in the transmission or reflection measurements. Such errors may be eliminated or greatly reduced by the proper use of filters, those being used which transmit freely at the desired wave-lengths and absorb as completely as possible at all wave-lengths of greater sensitivity.

(4) *Errors in the photometric scale.* By the photometric scale is meant that part of the apparatus by means of which the values of transmission or reflectance are obtained at any wave-length. In visual work the brightness may be varied by polarisation methods, by variable sectors, by varying the distance of a source from a surface, by absorbing wedges, and by various other means. The reliability of the values of transmission or reflectance that are obtained will depend, among other things, on how accurately the assumed photometric law is being obeyed.

The photo-electric method may be designed and used in a similar manner; that is, a null method or an equal-deflections method may be used, the intensity being varied and the spectrophotometric values being computed via the auxiliary photometric device, as in the visual method. In this case the same consideration must be given to the reliability of the photometric variable* as in visual work. However, the photo-electric cell may be used in a ratio-of-deflections method without auxiliary means of varying or measuring the intensity. The accuracy of the results then depends on how strictly the proportionality holds between the photo-electric current (as determined by the electrometer, galvanometer, or amplifying circuit) and the irradiation† on the cell. It is generally admitted that such proportionality cannot safely be assumed without test.

* The use of a rotating sector with a photo-electric cell is attended with some risk, unless the particular cell used has been shown by test to obey Talbot's law. This question has been considered by various investigators for many years. The following quotation is taken from a book entitled *Photo-electric Cells* by N. R. Campbell and D. Ritchie (Sir Isaac Pitman & Sons, Ltd., London, 1929), p. 193:

"The sector disc cannot be used unless Talbot's law is true, i.e., unless the time-average of the photoelectric current is determined wholly by the time-average of the incident light. The law is always true if the current is proportional to the light and sometimes when it is not (see G. H. Carruthers and T. H. Harrison, *Phil. Mag.*, **7**, 792 (1929)); but it is not true when proportionality fails because a gas-filled cell is being used very near its glow potential."

Incidentally, this book should be examined by all who are interested in the properties, use, and applications of the photo-electric cell. Its emphasis on accuracy throughout is to be highly commended.

† Following proposals made by Ives (H. E. Ives, "The units and nomenclature of radiation and illumination," *Astrophys. Journ.* **45**, 39–49 (1917)) and incorporated on pp. 173–5 of the O.S.A. spectrophotometry committee report already referred to, the more general terms of *radiant energy* (or simply *energy*), *irradiation*, and *radiance* are used, respectively, in place of *light*, *illumination*, and *brightness*, where the subject under consideration is of a more general nature than is covered by the usual photometric nomenclature, which, strictly, refers only to quantities detected and measured visually. To be consistent in this respect, the words *spectrophotometry* and *spectrophotometric* should not be used to apply to methods other than visual, even when such methods are used in the visible spectrum. This use of the words is so common, however, particularly as applying to photographic and photo-electric methods of measuring spectral transmission and reflection, that it seems preferable to use it in these connexions, rather than the more general terms, *spectroradiometry*, and *spectroradiometric*, which have been applied so generally to thermo-electric and bolometric methods and to measurements of spectral energy distribution generally.

(5) *Errors resulting from introduction of the sample into the beam.* In transmission measurements, because of thickness of the sample, lack of parallelism of the surfaces, or optical imperfection of one kind or another, the energy being used when the sample is in the beam and when it is out may be coming from different parts of the source. In this case error will be introduced unless the radiance of the source is uniform over an area sufficient to keep the source effectively unchanged when the sample is inserted. In reflectance measurements, the energy reflected is a function of the angle of incidence and of the angle of reflection. Apparent reflectances determined as a function of wave-length under varying conditions of irradiation and reflection cannot be expected to be identical, although they may be nearly so for highly diffusing surfaces. Such differences need not be considered as errors, but any spectral reflectance curve pertains strictly only to the particular conditions of irradiation and observation used. Unless those conditions are stated, the specification is incomplete, and a "complete record of a coloured sample" cannot be obtained until the apparent reflectance is studied as a function of wave-length for all conditions of irradiation and angles of observation. Two real sources of error may, however, be present: (1) The sample may not be subjected to the identical conditions of irradiation as the reference white, (2) where either the angle of observation or the angle of irradiation is notably different from zero, for example 45°, the reflected energy from all but the best diffusers is partially polarised*; and, unless this polarised component is properly directed, the polarising action of the dispersing prism will cause errors in the measured results.

One other effect should be noted, which, while not a true error, will prevent a reproducibility of "0·1 per cent." over a period of time unless properly controlled. This is the temperature effect. Most materials, both transmission and reflection samples, show important temperature variations at some wave-lengths, and the specification of spectrophotometric data is not complete unless the temperature at which they were obtained is stated.

In addition to the above kinds of errors, there may also be others, peculiar to the particular instrument or method, which must be carefully studied and eliminated (or corrections made) before any claim to high accuracy is justified. In any event the careful worker will assume nothing in respect to the accuracy of his spectrophotometer. In one way or another he will check the reliability of the values given by the instrument.

§ 3. SPECTROPHOTOMETRIC MEASUREMENTS WITH THE PHOTO-ELECTRIC CELL

Various ways of using the photo-electric cell to measure spectral transmission or reflection may be illustrated by noting briefly the methods used by those investigators who for one reason or another during the past twenty or thirty years have found it desirable to employ this relatively new spectrophotometric tool. In describing these methods it will, in general, be sufficient to note: (1) The quantity measured, (2) the wave-length range covered, (3) the kind of source used, (4) the

* Where completely diffused irradiation is used, or where the incident energy (whatever the angle) comes from two or more directions in such a way that the polarised components of the reflected energy properly compensate each other, the energy reflected at right angles to the surface will in general be unpolarised.

type of spectrometer, (5) the kind of photo-electric cell, and (6) the photometric method employed. The references mentioned should be consulted for further details.

One of the first spectrophotometric applications to which the photo-electric cell was put was the determination of the absorption of gases, particularly that of ozone. Von Halban* gives references to several investigators who carried on such work between 1901 and 1912. The absorption was determined as a function of wave-length between 185 and 300 mμ. As source either the quartz-mercury arc or the spark discharge of metals in air was used. The optical parts were of quartz or fluorite, and the cathodes of the photo-electric cells were of platinum or potassium. The photo-electric cells were connected to quadrant electrometers and the energy incident on the cells was taken as proportional to the deflections of the electrometer.

Another to make early use of the photo-electric cell for spectrophotometric measurements was Winther† in 1913, who determined the "extinction coefficients" of three fluorescent solutions. A quartz-mercury arc, quartz spectrograph, and potassium cell were used, and measurements were made at the mercury wave-lengths from 579 to 254 mμ. The cell was connected to a quadrant electrometer. Computation of the extinction coefficient at any wave-length was made from the observed rates of drift of the electrometer disk.

Perhaps the first to make extensive spectrophotometric use of the photo-electric cell was Hulburt‡ in 1915, who measured as a function of wave-length the absolute specular reflectances for 18° incidence of twenty-eight different metals, prepared in the form of plane polished surfaces. He covered a wave-length range from 180 to 380 mμ by steps of 10 mμ, using an end-on hydrogen discharge tube as source and forming the spectrum by means of a concave speculum-metal reflecting grating with the usual Rowland mounting. A sodium photo-electric cell was used with a fluorite window. The cell and the metallic mirror whose reflectance was desired were mounted in such a way that the cell could be exposed first to the incident energy of the desired wave-length and then to the same energy reflected from the mirror. The photo-electric current was measured by a ratio-of-deflections method with a Dolezalek quadrant electrometer. Exposures of fifteen seconds were given and the resulting steady deflections of the electrometer needle were noted, first for the incident energy direct and then for this energy reflected from the metal. The ratio of these deflections was taken as the reflectance of the metallic mirror for the 18° incidence.

Similar photo-electric measurements were made by Nathanson§ in the visible spectrum in 1916. He measured the reflectances of surfaces of sodium, potassium, and rubidium in contact with quartz for various angles of incidence and for radiant energy polarised both parallel and perpendicular to the plane of incidence. An

* H. von Halban, *Z. f. phys. Chem.* **96**, 214, footnote 2 (1920).

† C. Winther, "Über eine einfache Methode zur absoluten Messung von ultravioletter und sichtbarer Strahlung," *Z. f. Elektrochem.* **19**, 389–97 (1913).

‡ E. O. Hulburt, "The reflecting power of metals in the ultra-violet region of the spectrum," *Astrophys. Journ.* **42**, 205–30 (1915).

§ J. B. Nathanson, "The reflecting power of the alkali metals," *Astrophys. Journ.* **44**, 137–68 (1916).

incandescent lamp was used as source, with a prism spectrometer and a rubidium photo-electric cell. Measurements were made at five wave-lengths between 450 and 650 mμ. Either the steady deflection of the electrometer or the "first throw" were noted for definite short intervals of time. A linear relation was not assumed between the irradiation on the photo-electric cell and the resulting electrometer deflection; instead, the deflections were calibrated in terms of irradiation by means of nicol prisms and the cosine-square law.

The photo-electric cell was also used in a study of the reflectances and transmissions of sodium and potassium in contact with quartz in 1920 by Frehafer*, who made measurements at 10° incidence, with energy parallel and perpendicular to the plane of incidence, at the mercury wave-lengths from 546·1 to 253·6 mμ. A quartz-mercury arc and a quartz spectrograph were used. The same cell was used as had been used by Hulburt, but the photo-electric current was measured by the rate of fall of a sensitive gold-leaf electroscope. The cell was shown by test to give a linear relation between irradiation and photo-electric current.

One of the first applications of the photo-electric cell to colorimetric research was initiated in connexion with the colour standardisation programme of the Bureau of Standards. To supplement other spectrophotometric methods, particularly in the blue and violet spectral regions, Gibson† developed a photo-electric spectrophotometer for measuring transmission and diffuse reflection. A range from 380 to approximately 600 mμ was covered. Two potassium photo-electric cells were used in a sort of "Wheatstone-bridge" arrangement, a null method being employed and a Dolezalek quadrant electrometer serving as the indicator. For spectral transmission measurements, the amount of energy entering the spectrometer slit was varied by varying the distance of the source from the slit. The photo-electric current thus produced was balanced by the photo-electric current of the second cell irradiated by a small lamp. The two lamps were operated in parallel, with suitable resistances, on a storage battery. The transmission sample was then inserted before the spectrometer slit and the balance restored by moving the lamp toward the slit the necessary amount. The transmission was then computed from the inverse squares of the distances. Rotating sectors were used to extend the range of measurement. (Measurements with the rotating sectors served also to intercheck the reliability of Talbot's law and that of the inverse-square law.)

For the diffuse reflection measurements the lamp was brought close to the spectrometer slit and left stationary; by means of a mirror and lens the energy was focused upon the sample at approximately 45°, and the energy leaving the sample at right angles to its surface entered the spectrometer slit. Either the test sample or the reference white surface ($MgCO_3$ or MgO) could be brought into the beam before the slit. The photo-electric current was balanced by that of the second cell, irradiated by the small lamp through an adjustable slit and milk glass diffuser. When the electrometer balance was destroyed by interchange of the sample and reference white, it could be restored by varying the width of the slit before the

* M. K. Frehafer, "Reflection and transmission of ultra-violet light by sodium and potassium," *Phys. Rev.* (2), **15**, 110–25 (1920).

† K. S. Gibson, "Photoelectric spectrophotometry by the null method," *Bur. Stand. Scient. Papers*, No. 349 (Oct. 1919).

second cell; and the relative reflectance, for the particular angles of irradiation and reflection, was taken as the ratio of the slit widths. This method, while not as sound as the method used for the transmission measurements, proved fairly satisfactory.

The photo-electric null method described above was used to obtain published results for coloured glasses*, dye solutions†, and coloured papers‡, and was in routine use for test measurements from 1918 to 1923.

In the latter year it was superseded by a simpler and more rapid method § designed only for spectral transmission measurements and used continually from then to the present time. This is an equal-deflections method with a galvanometer and a single cell. The sample and a Brodhun sector are placed between two lenses used to focus the image of a gas-filled lamp filament on the spectrometer slit. With the Brodhun sector set at 100·0 the galvanometer reading is noted; the sample is then removed from the beam and the sector adjusted to give the same galvanometer reading as before. This sector reading is taken as the transmission of the sample. The lamp is operated on a storage battery. The working range of the method depends on the type of photo-electric cell, both potassium and caesium cells having been used.

The photo-electric cell has been used by von Halban in a series of investigations in physical chemistry, including studies of the validity of Beer's law, the influence of various factors on spectral absorption, the determination of constants of absorption, and so on. He has used the null method in two forms. In the first method || the photo-electric current produced by the incident energy was balanced by a current passing through a high resistance and produced by a variable and accurately known voltage. Equality of the two currents was indicated by the zero motion of a string electrometer. Either an incandescent light or a quartz-mercury lamp was used as source; dispersion was produced by interchangeable glass or quartz-fluorite optical parts; and both sodium and potassium photo-electric cells were used, made of uviol glass. A wave-length range from 300 to 630 mμ was found feasible with the incandescent source, which could be extended as far as 253 mμ by use of the mercury source. To measure transmittancy a cell containing the solvent was placed between the spectrometer and the photo-electric cell and the compensating voltage adjusted to give zero deflection of the electrometer. The solvent cell was then replaced by a similar cell containing the solution and the voltage again adjusted to give zero deflection. The ratio of the compensating voltages was taken as the transmittancy for the given wave-length.

This method was later revised¶. Two photo-electric cells were used, the second cell furnishing the compensating current in place of the variable voltage previously

* *Bur. Stand. Scient. Papers*, No. 349; *Bur. Stand. Techn. Papers*, No. 148.

† *Bur. Stand. Scient. Papers*, No. 440.

‡ *Bur. Stand. Techn. Papers*, No. 167.

§ K. S. Gibson, "Direct-reading photoelectric measurement of spectral transmission," *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **7**, 693–704 (1923).

|| H. von Halban and H. Geigel, "Über die Verwendung von photoelektrischen Zellen zur Messung der Lichtabsorption in Lösungen," *Z. f. phys. Chem.* **96**, 214–50 (1920).

¶ H. von Halban and K. Siedentopf, "Über die Verwendung von photoelektrischen Zellen zur Messung der Lichtabsorption in Lösungen, II," *Z. f. phys. Chem.* **100**, 208–30 (1922).

used. The method was, in fact, similar to the "Wheatstone-bridge" arrangement described above. The string electrometer served as a null instrument to indicate equality of the two photo-electric currents. Radiant energy from a quartz-mercury arc was dispersed by means of a quartz monochromator. The exit beam was then split into two beams by means of a transparent quartz plate, the transmitted beam passing through the absorbant to one cell and the reflected beam passing to the compensating cell. In the beam with the absorbant was placed a Goldberg "neutral" wedge and a variable sector. The sector was used primarily for absolute measurements. Transmittancy was determined, for example, by taking the ratio of the sector readings, adjusted respectively to give no deflection of the electrometer both when the solvent and when the solution were in the beam. The wedge, whose transmission was calibrated as a function of wave-length by means of the sector, was used mostly for the measurement of small differences in transmittancy. Measurements could be made at the mercury wave-lengths from 579 to 254 mμ. This method of use of a single source eliminated errors due to small fluctuations in the source.

These methods were used in several investigations, the various publications being listed in two of the more recent papers*. In this last paper the grey wedge was combined with the single-cell arrangement described above.

In 1925 Müller† devised apparatus for measuring spectral transmissions via a photo-electric cell and string electrometer, which avoided various possible errors connected with the latter when used as a ratio-of-deflections instrument. Energy from a source was dispersed by a constant-deviation spectrometer, and that of the desired wave-length was incident upon a photo-electric cell placed at the ocular slit. The photo-electric current thus produced was indicated by the deflection of the electrometer string, which deflection was magnified and recorded photographically in a manner similar to that used in the Koch registering microphotometer. Before the entrance slit of the spectrometer could be placed either the sample being measured or a rotating sector designed to give 100, 80, 60, 40, 20, and 0 per cent. transmission. At each wave-length the electrometer deflection was recorded first when the sample was in the beam and then when the sector was in the beam at each of the six positions respectively. The transmission of the sample at that wave-length was then obtained by interpolation on the photographic plate.

Further details and revisions of the apparatus are given in subsequent publications‡. The method has also been used in the determination of absorption and reflection characteristics of thin films in the ultra-violet, in various photometric problems, in the registration of spectrograms, and in determining the decay curves of luminescent and radioactive materials.

Two other instances where the photo-electric cell has been used in spectro-

* *Proc. R. S.* **116**, 153–62 (1927); *Z. f. Elektrochem.* **34**, 387–93 (1928).

† C. Müller, "Registrierapparat zur direkten Aufnahme von Durchlässigkeitskurven absorbierender Substanzen und Spektraler Effekte," *Z. f. Phys.* **34**, 824–32 (1925).

‡ C. Müller, "Über die Ausschaltung von Störungen und Empfindlichkeitsabweichungen bei registrierender Photometrierung," *Z. f. techn. Phys.* **9**, 154–7 (1928); C. Müller and R. Frisch, "Registrierendes Präzisionsgerät für sehr schwache Ströme (Lichtintensitäten, Ionisationsvorgänge u.s.w.)," *ibid.* **9**, 445–51 (1928).

photometric measurements may be noted, before considering the methods that have been developed with the amplified photo-electric current.

The first case is an illustration of the use of the photo-electric cell for measuring the energy distribution in certain fluorescent spectra. The method is described by L. Taylor*. A potassium cell was used and the photo-electric current was measured by the rate of drift of the disk of a Compton electrometer. The energy distribution of the fluorescent light was compared with that from a standardised incandescent lamp, the two energies traversing the same path through a prism spectrometer.

The second case is an instance of an "abridged" spectrophotometric method, wherein the energy from the source, instead of being dispersed by a spectrometer, is isolated by a series of filters. The instrument is known as the T.C.B. photo-colorimeter and was designed by Toussaint†. The energy from an incandescent source is collimated and after passage through the filter is incident upon the sample. The reflected energy from the sample irradiates a potassium photo-electric cell and the deflection produced in a galvanometer is compared with that produced from a reference white under the same conditions. The six filters used are Wratten filters and the values obtained are plotted at the following respective wave-lengths: 400, 450, 530, 580, 620, 700 mμ. The instrument does not, of course, give the exact analysis possible with a true spectrophotometer and, as in many colorimeters, the question of permanence and reproducibility of the filters must be considered. Likewise, the method is not so truly independent of the energy distribution of the source and the spectral sensitivity of the photo-electric cell as in a real spectrophotometer. However, the apparatus is relatively simple, and the method is doubtless of value in control work. It is applicable likewise to transmission measurements.

Amplification has been applied to the photo-electric current for many years and, particularly recently, for a great variety of purposes. There are now several laboratories making use of amplified-photo-electric spectrophotometry.

The Electrical Testing Laboratories‡ has used Gibson's equal-deflection method for several years in the measurement of spectral transmission. The only essential change in the method, as described above, consisted in amplifying the photo-electric current. The published results show the method used from 420 to 690 mμ but, as in all cases, the possible range depends on the type of cell used.

An adaptation of the Yvon polarisation spectrophotometer to photo-electric measurements has been made by Tardy§. A potassium cell is used which, with the prismatic dispersion and incandescent source, gives a wave-length range from 400 to 650 mμ. In the Yvon spectrophotometer a beam of energy is divided into

* L. Taylor, "A comparison of three spectrophotometric methods," *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **14**, 332–6 (1927).

† Obtainable from the Laboratoire de Contrôle et d'Essais pour les Textiles, Fils et Tissus (143, Rue d'Alésia, Paris). See description in *Cotton*, **91**, 981–3 (August, 1927).

‡ C. H. Sharp, "Various applications of the photoelectric cell with amplifier to photometry," *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **13**, 304 (1926); see also *Trans. Illum. Eng. Soc.* **23**, 419–27 (1928).

§ L. H. Tardy, "Le remplacement de l'œil par la cellule photoélectrique sur les spectrophotomètres visuels," *Rev. d'Optique*, **7**, 189–95 (1928).

two parts, each of which passes through a pair of nicol prisms. As used with the photo-electric cell, first one beam and then the other is allowed to fall on the photo-electric cell, both beams having the same wave-length and the same state of polarisation. The resulting currents, amplified, are indicated by a galvanometer. The method is an equal-deflections one. In measuring transmission, the sample is placed in one of the beams and the adjustable nicol in the other beam is rotated until the galvanometer gives the same deflection for either beam. The sample is then removed and the nicol further adjusted until, again, both beams give the same deflection. The transmission is computed from the sine-square relation. Constancy of source is considered necessary only during interchange of beams.

A photo-electric spectrophotometer has been devised by A. H. Taylor* for the measurement of spectral transmission. A caesium cell is used which, with the incandescent source and glass-prism spectrometer, enables measurements to be made throughout the visible spectrum from 400 to 760 mμ. The caesium cell is placed beyond the telescope slit, and the photo-electric current is amplified. "Between the dispersing prism and the ocular telescope a housing was built. This contains a movable 45° mirror by means of which an opal-glass disk immediately above is imaged in the ocular telescope. Above this opal-glass is placed a movable tungsten lamp which illuminates it. The range of movement of this lamp is sufficient to make a change of 6 to 1 in the illumination of the opal-disk. Additional range is provided for by a sectored disk placed between the ribbon-filament lamp and the collimator slit.... When making a photometric balance the photoelectric cell is first exposed to the monochromatic light, and the rheostat is adjusted to make the galvanometer current approximately zero. Then the 45° mirror is moved into position to obscure the monochromatic light and substitute the image of the opal-glass disk. The movable lamp is adjusted until the galvanometer deflection is the same as before. If the balance remains unchanged when the monochromatic light is again exposed, the distance of the lamp from the opal glass is read off from a scale. When the spectral transmission of a colored glass is to be measured, the glass is placed between the ribbon-filament lamp and the collimator slit. Photometric balances are made at desired wave-length intervals with and without the glass interposed." Results obtained by this method have been published† in connexion with an inter-laboratory comparison of photometric filters.

An outstanding advance in speed of determination and in automatic operation has been contributed by Hardy‡ in his "recording photo-electric color analyser." "The operation of this instrument may be briefly described as follows: The specimen and a surface of magnesium carbonate are illuminated from opposite sides of a ribbon filament tungsten lamp. Beams of light from the specimen and from the magnesium carbonate standard are alternately admitted to the slit of a dispersing system. A narrow band of each of the spectra thus formed falls successively on a photoelectric cell and causes a pulsating current in the cell circuit when the two

* A. H. Taylor, "Photoelectric spectrophotometry," *Journ. Frank. Inst.* **206**, 241–2 (1928).

† *Trans. Illum. Eng. Soc.* **24**, 153–207 (1929).

‡ A. C. Hardy, "A recording photoelectric color analyser," *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **18**, 96–117 (1929). The parts quoted are taken from pp. 96–7 of this paper. See also *ibid.* **16**, 119 (1928) and *Soc. Automotive Eng. Journ.* **25**, 39–43 (1929).

beams are of unequal intensity. This current is amplified by pliotrons and the alternating component is applied to the field coils of a small motor, the armature being supplied from an independent source of the same frequency. With this arrangement, the armature rotates in one direction when the beam from the specimen is more intense and in the opposite direction when the beam from the standard is more intense. When the intensities are equal, the field current ceases and the motor stops. By causing the motor to control a diaphragm which varies the illumination on the magnesium carbonate, the intensities of the two beams are automatically balanced. A pen operating on a rotating drum records the position of this diaphragm while the rotation of the drum changes the wave length of the spectral band admitted to the photoelectric cell. In this way, a complete spectrophotoelectric curve for the entire visible spectrum is traced in approximately thirty seconds."

In the revised model now being manufactured by the General Electric Company the source and cell have, in effect, been interchanged, so that the beam undergoes the prismatic dispersion before being incident upon the sample. The instrument will measure spectral transmission as well as spectral reflectance.

A photo-electric spectrophotometer has been developed by the American Photoelectric Corporation*, Eimer and Amend being the manufacturer and distributor. The photo-electric cell, amplifying circuit, and photometric device are contained in separate units and may be combined with any spectrometer and any source as desired, for measurements in the infra-red, visible, or ultra-violet. The apparatus has "as essential parts (1) a carrier for the sample, (2) a light source operated by a storage battery, (3) a spectrometer to segregate the lines or bands of the desired wave length, (4) the case containing the photoelectric cell unit, electrical circuits, amplifiers, control panels, etc., (5) a galvanometer, and (6) a Wheatstone bridge, usually one of the Kohlrausch type."

"To make a reading on any material at any desired wave length, it is necessary only to balance an electrical circuit by turning a dial similar to those on radio sets, and then, after interposing the material under examination, again to balance the circuit by turning another dial on which is read directly in per cent. the proportion of the total light of that particular wave length which is transmitted or reflected by the material."

Another automatic photo-electric spectrophotometer, designed to plot rapidly the spectral reflectance curve, has been developed by Mulder and Razek†. "The new color analyzer is portable and is built into a box about the size of a large suitcase. It can be operated either by connexion to any electric light socket or from a suitable bank of batteries.

"The sample to be tested is placed over a small rectangular opening on the top of the box where it is illuminated by a powerful source of light. The light reflected

* *American Photoelectric Corporation Bulletin* No. 101. The quotations are taken from this bulletin. See also H. D. Ellsworth, M. Barnard, and P. McMichael, "Photoelectric color measurements," *Oil and Fat Industries*, **7**, 15–19 (January, 1930).

† P. J. Mulder and J. Razek, "A portable recording and indicating color analyzer," *Journ. Opt. Soc. Amer.* **20**, 155–6 (April, 1930). See also "Automatic color analyser," *Textile World*, p. 54 (Feb. 22, 1930), from which the quotation is taken.

perpendicularly from the sample is admitted to a spectroscope in which it is separated into its component colors. A selected portion of the dispersed light is then allowed to pass into a photo-electric cell, the very feeble current passed by this cell as a result of the light falling upon it being amplified about a million times. This is done by means of a special amplifier, known as a 'bridge grid resistor amplifier' developed for the particular purpose.

"The amplifier employs two vacuum tubes such as are used in the last stage of many radio sets, with certain adaptations which greatly increase their sensitivity, The amplifier current is indicated on a sensitive galvanometer whose reading can be noted on a scale on the front of the machine and at the same time recorded on a photographic film. By turning a small crank, different portions of the spectrum are successively admitted to the photo-electric cell until the entire spectrum has been covered, while the photographic film is moved through a corresponding distance. Coordinate lines and an identification number are printed on the film in a separate compartment of the machine."

It is quite possible that other photo-electric spectrophotometers have been developed and used, which have been inadvertently omitted in the résumé above. Those described will, however, serve to illustrate the great variety of methods that can be used in this application of the photo-electric cell. No reference (with one exception) has been made to the many cases where photo-electric methods have been used to measure the densities of photographed spectra; such data are primarily photographic. Nor have those cases been noted where the photo-electric cell has been used to measure the relative spectral energy distribution of the stars or the sun; these instances will doubtless be considered in connexion with the applications of the photo-electric cell to astronomical measurements. Likewise, the determination of the colour temperature of incandescent lamps will probably be discussed along with the many other uses of the photo-electric cell in photometry, and is accordingly excluded from the present paper.

It is too soon to tell how satisfactory these new rapidly operated photo-electric spectrophotometers will prove in practice. It may again be noted that they are, in common with all spectrophotometric methods, liable to the various errors noted in the previous section, and that the values of spectral reflectance obtained are strictly characteristic of the sample only for the particular experimental conditions of irradiation and observation that are being used—which, furthermore, are in some cases none too precisely defined. Ideas for eliminating some of the errors and uncertainties in spectrophotometric measurements, while utilising the speed of operation possible with the amplified photo-electric current, have been briefly noted*, but have not yet been put in operation. It is understood, also, that a new photo-electric spectrophotometer has been developed at the National Physical Laboratory, but details of the method have not come to our attention.

In conclusion, it may be noted that the rapid progress now being made in photo-electric spectrophotometry is very gratifying. Undoubtedly, the more tedious methods will be gradually superseded over the spectral range for which

* K. S. Gibson, "Apparatus for accurate and rapid measurement of spectral transmission and reflection," *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **18**, 166 (1929).

the photo-electric method can be made applicable. This will not be done, however, at least by those to whom accuracy of data is the primary consideration, until the new methods can be demonstrated to have an equal reliability with these earlier ones. As previously noted, it is customary to compare the new photo-electric methods of spectrophotometry with visual methods, to the great disparagement of the latter. It is, perhaps, worthy of mention, however, that in several instances those who have developed or are using amplified-photo-electric spectrophotometers have tested the reliability of their instruments by means of glasses whose spectral transmissions have been determined by the visual method as installed and used in the Colorimetry Section of the Bureau of Standards*. Such checking of accuracy is, of course, a very desirable procedure, and indicates that there are many who realise the possibilities for error in the new instruments. It is hoped that this paper may help those who are not familiar with the subject to guard against such errors. If it seems that too much emphasis has been given herein to the possible limitations of photo-electric spectrophotometers as compared with their undoubted advantages, we can only say that such advantages are being more than adequately stated by those who are developing and selling the instruments. Their limitations are, however, none too well known and it will be of real advantage to all concerned if such knowledge can be more widely disseminated.

* H. J. McNicholas, "Equipment for routine spectral transmission and reflection measurements," *Bur. Stand. Res. Paper* No. 30 (1928).

SPECTROPHOTOMETRIC ABSORPTION MEASUREMENTS

By D. S. PERFECT, M.A., D.Phil., F.Inst.P.,
Optics Department, The National Physical Laboratory.

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ABSTRACT. The paper describes various methods of photo-electric spectrophotometry which have been developed, and discusses their relative merits, chiefly from the point of view of the detecting system. The methods dealt with are those depending on (*a*) the absence of change in the deflection of a quick-period electrometer, (*b*) the absence of change in the deflection of a slow-period electrometer, (*c*) relative deflections in equal times, (*d*) relative times of equal deflections, (*e*) zero deflection where two cells are used in opposition, and (*f*) zero deflection where two beams are rapidly alternated, and the photo-electric current is amplified, rectified, and indicated by a galvanometer. Of these methods (*a*), (*b*), (*c*) and (*d*) are suitable for use with steady sources of radiation, (*a*) and (*e*) are suitable for moderately unsteady sources, and (*f*) is suitable for very unsteady sources. In connexion with one of the methods special types of rotating sectors are described.

§ 1. INTRODUCTION

THE present paper discusses the photo-electric methods which have been used in the National Physical Laboratory since 1924 for measurements of the absorption of monochromatic radiation, and particularly of ultra-violet radiation. There are many points having a bearing on the general problem of which the interest is mainly optical or mechanical. With these it is hoped to deal in a further paper. The present discussion is limited to those aspects in which the use of photo-electric cells forms the chief part.

From the outset it was decided to employ methods in which the cell is used only as a detector of small differences. Consequently linearity of the current-illumination characteristic is not necessary. The most important desideratum is sensitivity and therefore gas-filled cells have been used throughout the work.

It was anticipated that when working in the ultra-violet the chief difficulties would be due to unsteadiness in the available sources of radiation. The first methods tried were therefore designed to reduce as much as possible the time of comparison of the two beams of radiation (one passing through the specimen whose absorption is to be measured, the other through a standard of absorption). A detector having rapid action was thus necessary, and was secured by employing the Lindemann electrometer which had recently been perfected.

§ 2. METHOD OF "SYNCHRONISING KICKS"

The apparatus employing the method adopted at this stage is shown diagrammatically in Fig. 1. Radiation from the exit slit s of a monochromator* μ is collimated by the lens L and directed on to the cell C by either of the two prisms P_1, P_2. P_2 is fixed; P_1 is movable (parallel to the hypotenuse) so that in one position it intercepts and reflects the radiation, in the other the radiation is allowed to travel on to P_2. In the absence of any absorbing specimens the total radiation reaching the cell is unchanged by moving P_1, but if a specimen X and standard S of slightly

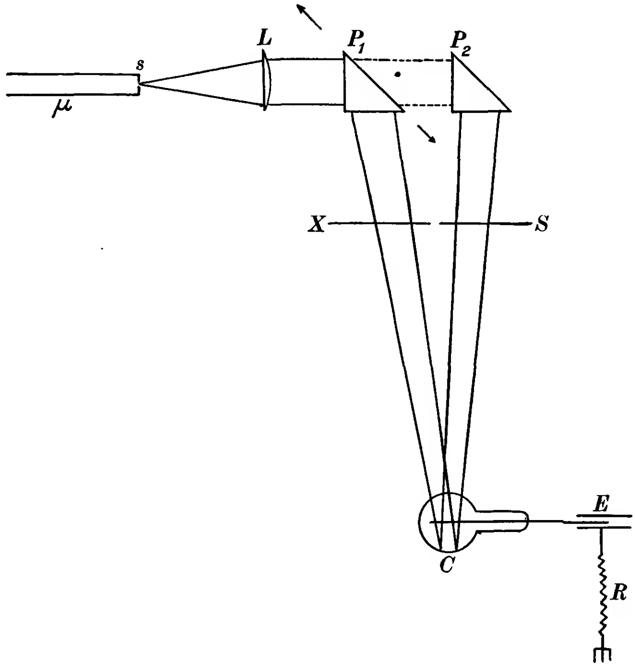

Fig. 1.

different absorptions are placed in the paths of the two beams the intensity of radiation will change abruptly if P_1 is moved rapidly in or out of the beam. The photo-electric current is measured by the maximum deflection acquired by the Lindemann electrometer E, the needle of which is connected to earth through a xylene-alcohol leak R†, so that the abrupt change in the radiation is accompanied by a sudden kick in the needle of the electrometer. This kick can be identified after one or two trials, even in the presence of chaotic movements, by the fact that it synchronises with the movement of P_1, and can be reduced to zero by suitably

* The monochromator consists throughout of two spectrometers in series. Such a system is necessary (particularly in the ultra-violet) to reduce the stray light to negligible magnitude.

† No troubles due to polarisation have been experienced in using this type of leak such as have been found by some workers.

adjusting S. For this purpose S must therefore be continuously variable and this condition was fulfilled by the use of wedges and inclined plates. The method is essentially similar in principle to that employed in the densitometer designed by Dr Dobson*.

The detecting system was designed as a portable unit which has been valuable for this and other photometric work. A photograph of this part of the apparatus is shown in Fig. 2. C is the photo-electric cell, E the electrometer, H a knurled head for rotating the needle of the electrometer, T_1, T_2 the H.T. terminals to the electro-

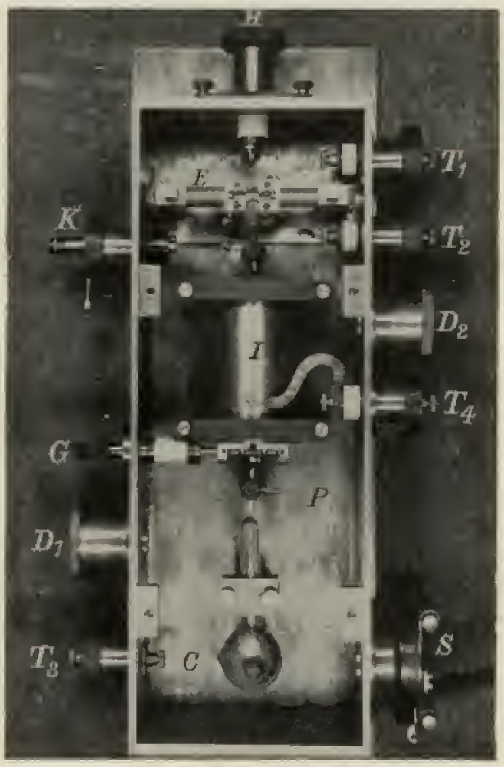

Fig. 2.

meter, T_3 the H.T. terminal to the cell, D_1, D_2 drying chambers, K an earthing key which can be operated manually or electrically, and S a shutter operated pneumatically. The xylene-alcohol leak, not shown in the photograph, may be inserted next the cell C and connected to the system by means of the peg P. At the suggestion of Dr E. A. Owen an ionisation chamber I, coated with uranium oxide, was incorporated in the apparatus; T_4 is the H.T. terminal to it. The exposed area of the uranium oxide could be varied by rotating a concentric cylindrical shield by means of a tangent screw operated by the head G so that, if the ionisation current was opposed to the photo-electric current, a balance could be obtained. Then by dis-

* G. M. B. Dobson, "A flicker type of photo-electric photometer giving high precision," *Proc. R. S.* **104**, 248 (1923).

pensing with the leak to earth the method was convertible into a null method. After giving it a fair trial the use of the ionising chamber was abandoned because, though otherwise satisfactory, a persistent and irremediable small kicking of the electrometer was traced to it. When the null method was taken up at a later stage, as described below, a second photo-electric cell took the place of the ionisation chamber.

§ 3. METHOD OF "SLOW SHIFTS"

Although, as stated above, difficulty was anticipated in obtaining a sufficiently steady source, subsequent work showed that the mercury arc was in fact very steady, not only in respect of the mean value of the intensity over an extended time, but in the absence of flicker detectable by the Lindemann electrometer. Now the mercury arc provides enough sufficiently intense spectral lines to enable many of the important types of absorption spectra to be plotted without interpolating with lines of intermediate wave-lengths*, and, contrary to expectation, the technique appropriate to steady conditions took as important a place as that demanded for unsteady sources. For this reason it was possible to abandon the method of synchronous kicks and replace it by one in which slower transitions were used. This change was in any case necessary because the first method, excellent as it was where the radiation was sufficiently intense, was too insensitive for use with the fainter mercury lines, or near the end of the spectrum of a filament lamp (which in the near ultra-violet is used to fill in the gaps in the spectrum of the mercury arc), or when the absorption of the specimen was great. In order to avoid the "creeping-home," which is the price paid for increasing the sensitivity by increasing unduly the resistance of the leak, the Lindemann electrometer was replaced by a Compton electrometer.

The apparatus at this stage is shown in Fig. 3. The prisms are dispensed with and X, S (specimen and standard) are moved alternately into the beam. The method of adjusting S so that $S = X$ was no longer used as it was only essential in the

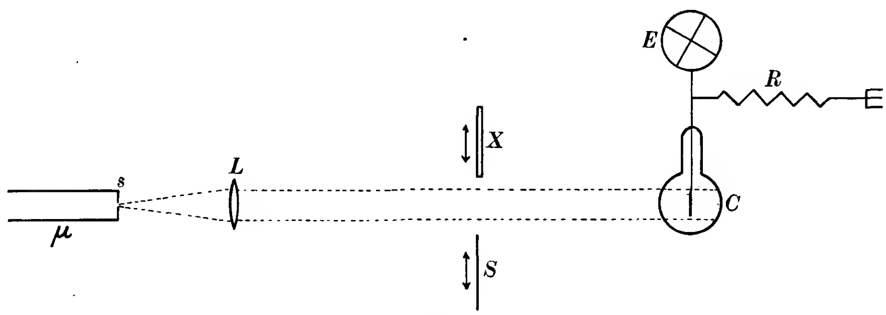

Fig. 3.

synchronising kick method. The necessity of making $S = X$ had precluded the use of a radial sector disc as standard since it is difficult to determine accurately the aperture of a continuously variable sector while it is running. It now became possible to use as a standard a sector disc of fixed aperture; this has the great advantage that

* The use of the mercury arc as source has in any event the further advantage that wave-length calibration and slit-width correction are unnecessary.

it is perfectly neutral and may be calibrated by purely geometrical measurements. Therefore instead of making S continuously variable it could be given a discrete series of values by means of a set of sectors of fixed aperture. In measuring X, the two members of the series were selected whose equivalent absorptions lay on either side of that of X. These were successively interchanged with X and the shifts (relatively slow shifts instead of rapid kicks) were measured. Then the value of X is given by interpolation. (If, instead of interpolating over a small range, X was evaluated by assuming linearity over the entire range, errors of more than 2 per cent. occurred.) This method was satisfactory at certain wave-lengths, but again the sensitivity was insufficient for universal use.

§ 4. METHOD OF EQUAL TIMES

In order to improve the sensitivity sufficiently, the leak to earth was discarded and the principle of observing changes in a steady deflection was abandoned. Before taking this step the magnitude of the leak resistance was increased until the method became unwieldy. After discarding the leak the photo-electric currents were measured by the deflection acquired by the Compton electrometer in a given time of irradiation of the cell. The optical system was still the same as that shown in Fig. 3.

In order to obtain exact reproducibility of the time of exposure, a special shutter was operated by an astronomical clock and was designed so that, to suit the intensity of the radiation, the exposure could be given any desired value between about 15 seconds and zero. This method gave good results but was eventually abandoned for the following reasons. In the first place the manipulation of the clock in a completely darkened room necessitated the help of a second operator (in the other methods, although the number of controls was somewhat large, a single operator could manage the apparatus). Secondly, in order that inaccuracy in reading the deflections should produce only a small percentage error, the deflections had to be fairly large, and when working with radiation of low intensity this meant times of exposure so long that uncertainties due to irregularities in dark current, natural leak of the insulated system, and any unsteadiness of the source became relatively serious.

§ 5. METHOD OF EQUAL DEFLECTIONS

It was found that better results were obtained, and could be obtained by only one operator, if the photo-electric current was determined by measuring on a stop-watch the time taken for the spot of light to pass between two fixed marks. The optical system is still that shown in Fig. 3. The "scale" consists of a number of rhombs whose diagonals are 2 cm. long, placed end to end as shown in Fig. 4; the two positions of the moving fiducial line at which the times are taken may be A, B; A, C; A, D;...that is, the measured drift is that multiple of 2 cm. most appropriate to the available energy. The initial undisturbed position is shown at O and is chosen sufficiently far from A (in practice about 8 cm.) for the attainment of a steady rate of drift at A. The setting is similar to the ordinary type of cross-wire setting. It is found that, when the rate of drift is neither too fast nor too slow (rates of between

8 cm. and 2 cm. in 20 seconds were found very satisfactory*) the time of passage can be measured by a skilled observer with a reproducibility of the order of 0·1 sec. For a total time of 20 seconds this means a precision of 0·5 per cent. With the method of equal times, to attain this precision for a deflection of 2 cm. the position of the fiducial line on the scale must be read to 0·1 mm.—a feat impossible without the use of a coincidence method (involving the use of movable cross-wires) and a vernier.

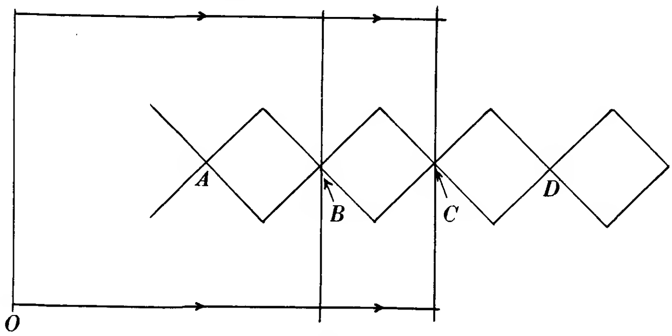

Fig. 4.

With this method the making of a single observation takes at least 60 seconds, including the reading and recording of the time. The method is therefore much slower than that of the "synchronising kicks" or of the "slow shifts," and hence at one period both methods were used concurrently for different intensities of available radiation. However, in view of the trouble of maintaining the two detectors, and of switching over from one to the other, it was ultimately found to be more economical to retain only the more sensitive method and to cut down the stronger radiations as required. From the fact that they were successively abandoned it must not be inferred that the various methods previously used were not found to work well. For the purposes of certain measurements they were excellent, and have been subsequently employed in other types of work in this Laboratory. The method of timing between fixed positions has been in use for carrying out many tests during the last two or three years and has proved very reliable. It is still employed for most of the ultra-violet test work. Reliable as it is, however, it suffers from certain defects. Firstly it is applicable only when the source of radiation is reasonably steady, and thus only gives a partial solution of the general problem. Secondly it gives no means of observing the behaviour of the source. When a steady deflection method is used fluctuations of the source are immediately made manifest as fluctuations in position of the spot, but it is impossible to detect by eye small changes of velocity of a moving spot. The only test of the steadiness of the source is the mutual consistency of a number of observations. Ten observations are usually taken for this purpose; this means that the observations necessary to establish the transmission at each wave-length occupy at least 10 minutes under the most favourable conditions.

* For feeble radiation the rate is inevitably much slower; when the radiation is strong it can be diminished by filters until the rate is reduced to about 8 cm. in 20 seconds.

§ 6. NULL METHOD EMPLOYING TWO BALANCED CELLS

In order to improve the technique in respect of the considerations just mentioned, two additional methods have been developed. In the first of these, two cells C_1, C_2 (Fig. 5), are balanced one against the other, the common electrode being connected to the quadrant of a Compton electrometer E. The other components of

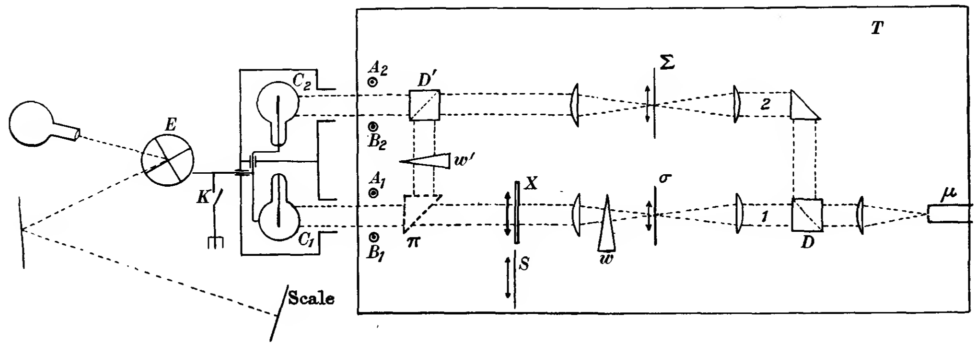

Fig. 5.

the equipment were mounted on the steel table T for the sake of rigidity. The optical system employed in the methods previously described (see Fig. 3) is here modified by the introduction of an auxiliary beam of light so that two beams 1 and 2 are produced simultaneously by the special dividing prism D*. (The two beams in

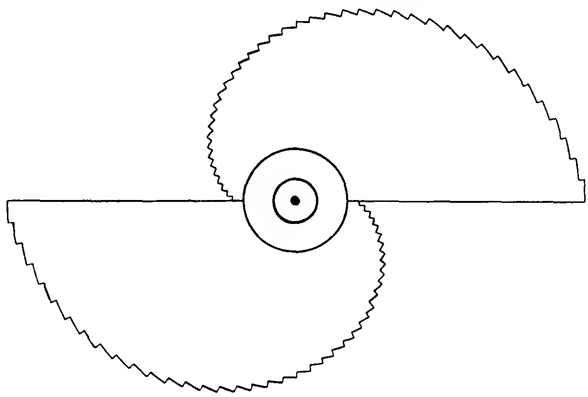

Fig. 6.

a previous method (Fig. 1) were produced successively instead of simultaneously because a saving in energy is thereby effected.) Simple substitution of specimen X and standard sector S is made (as described in § 3) in the path of the beam. The toothed disc Σ (shown in plan in Fig. 6), comprising essentially a group of rapidly

* This prism, which has not been previously described, was designed for another purpose by Mr J. Guild. It consists of two 45° prisms fitted in optical contact to form a cube, the interface being divided into strips about 1 mm. wide, which alternately reflect and transmit the light, so that the entire cross-section is treated in a uniform manner.

changeable radial sector discs, the transmission of which proceed from 0 to 100 per cent. in steps of 2·5 per cent., is placed in the path of beam 2 which is focussed so that all the energy is confined within the dimensions of one tooth. The transmission is given the value as near to that of X as Σ will give by sliding Σ laterally. Exact balance is attained by adjusting the optical wedge w placed in beam 1. It is convenient, before this adjustment is made, to balance any dark current which may be present. This is accomplished by lighting one or other of the two small lamps A_1, A_2, the brightness of which can be suitably adjusted. B_1, B_2 are two small lamps by means of which return of the electrometer to zero position can be accelerated.

Having attained a balance, S is substituted for X (the value of S nearest to X being chosen by making $S = \Sigma$). The balance is destroyed by the substitution and is restored by adjusting the position of the non-radial sector σ (shown in plan in Fig. 7) the transmission of which varies in a calculable manner from 100 per cent.

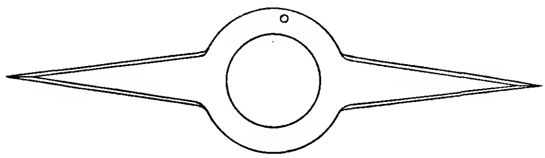

Fig. 7.

at the tip to 80 per cent. near the centre. The sector σ is mounted on a slide and its position is used as a scale on which is measured the relatively small difference $S \sim X$. The sectors S and σ are run at very different frequencies to avoid any slow pulsations of "intensity" in beam 1.

The apparatus is sufficiently sensitive to enable an accuracy of 0·1 per cent. to be attained in the green region of the spectrum, using a filament lamp as source. It was found however that before such accuracy could be reached one important precaution (apart from the numerous optical precautions) needed to be taken. It was necessary that the state of balance should not be disturbed throughout the course of a single determination, so that in effect reliance was placed on the principle that if, during a sequence of operations in which A is changed to B, a steady state depending on the value of A is maintained continuously, then A is equivalent to B. If, for example, the light was excluded from both cells while σ was being correctly adjusted, or, if the cells were earthed and irradiated while the difference $S \sim X$ was uncorrected, the former state of balance was not subsequently resumed by the cells. The disturbance was not very large, but might easily amount to, say, 0·5 per cent. To maintain the balance undisturbed a dividing prism D'* was introduced in beam 2 (Fig. 5) which sends half the energy of beam 2 in a component beam at right angles to beam 2 and directed towards beam 1. This component either crosses beam 1 and proceeds into space, or may be caught by a prism π and directed on to cell C_1. By means of a wedge w' the intensity of this component may be adjusted until the cells are balanced. The prism π is moved by vertical translation so that the beam directed by it on to C_1 is not displaced by the motion. If we assume, as is approximately true, that the energy density is uniform over the cross-sections

* This prism is similar to D, but the direction of the strips is at right angles to that in D.

of the beams, then, if the energy in beam 1 is equal to the energy in the component of beam 2, no matter how slowly the prism π is moved the total energy reaching cell C_1 is unchanged. Thus even the act of moving the prism into position will not upset the balance. The adjustments of σ may be made while π is operative; when they are completed π is withdrawn and a final small adjustment given to σ. By this procedure the reliability of the measurements was much increased.

The method of balancing two cells has been found preferable to that described in § 5 in the following respects. Fluctuations in intensity of the radiation of the mercury arc are almost entirely compensated. Any lack of steadiness, due to imperfect compensation or variation in high potential, is immediately visible, so that by choosing suitable times the required value of the transmission can be established by at most one repetition of measurement. The use of a timing device is avoided, and also the fatigue which accompanies protracted work involving the careful judgment of coincidences, and with it the necessity for the same degree of skill in observing.

On the other hand, the method is not free from certain defects. Although they are made visible, secular changes due to variations in the high potential accumulators and other causes cannot be avoided; and, owing to the lack of identity of the two cells, complete compensation of fluctuations of the radiation is not possible, so that the method does not effectually solve the problem of using unsteady sources. For instance, if a carbon or tungsten arc is used as source, steadiness is often maintained for periods of a few seconds, but sudden fluctuations of large magnitude are frequent.

§ 7. NULL METHOD EMPLOYING A VALVE AMPLIFIER

An attempt to remedy these disadvantages has been made in the development of the second of the two methods referred to at the beginning of § 6. The general principle of the method is described in another paper*. The system as applied to the present purpose has two modifications which differ in respect of the method used to vary the intensity of the comparison beam with which measurements are made. It is easy to see that with this type of detector it is impossible to use a rotating sector or system of sectors for compensating a change of intensity in one of the beams and restoring a balance. Consequently it is necessary, most unfortunately, to employ other means. Two methods are employed, the one depending on the inverse square law, the other on the use of an optical wedge. The choice between the two is guided by the particular circumstances. The wedge is mechanically simpler, and is satisfactory in the visible spectrum, but can be replaced by the alternative method for work in the ultra-violet.

The two systems are illustrated in Figs. 8 and 9, the first of which shows also the detecting system. In Fig. 8 two components of the radiation diverging from the monochromator μ are reflected from the prisms P_1, P_2 and illuminate, in the one case directly and in the other after reflection at the mirror M, the two circular apertures a, b (1 cm. in diameter) in the templet plate t. These apertures serve to

* G. M. B. Dobson and D. S. Perfect, "A method of comparing very small amounts of light by means of a photo-electric cell and a valve amplifier," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 79 (1930).

define exactly* the cross-sections of the beams which, emerging from them, fall on the rotating sector disc *d* (see also Fig. 8 (*a*)). They are then directed on to the cell *C* in rapid alternation by the prisms P_3, P_4. The concave lens *L* serves to spread out the beam over the sensitive area of the cell. Departure from equality of intensity in the two components produces a ripple in the photo-electric current which is amplified by the amplifier *A*, rectified by the commutator *k*, and indicated by the galvanometer *G*. Equality of intensity can be secured by varying the distance of the

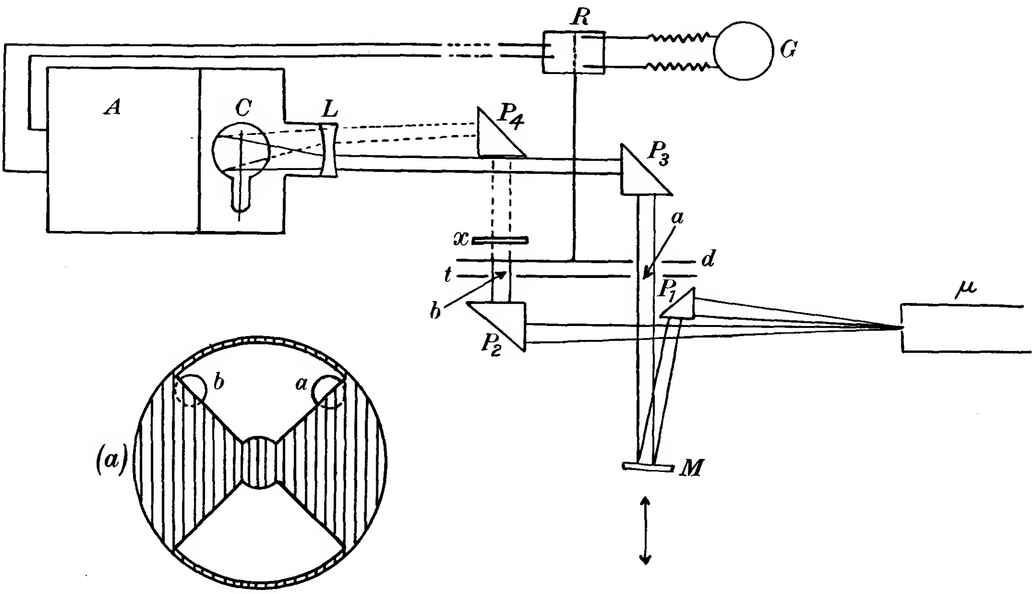

Fig. 8.

mirror *M* from *a* and μ until the galvanometer deflection is zero. If when this is done an absorbing specimen *X* is inserted in one beam, the equality of intensity can be restored by adjusting *M*, and the transmission of *X* calculated from the position of *M*.

In Fig. 9 the prism P_1 is reversed so that the radiation reflected by it passes straight to the aperture *a* and to the optical wedges *w* placed behind the rotating disc *d*. The remainder of the system is identical with that described above. In order that reliance should be placed on the absolute values given by the above methods of measurement, intercomparison and independent calibrations are necessary. But the equipment enables work to be carried out with quite unsteady sources, such as the tungsten and carbon arcs, and thus makes it possible to fill in the gaps between the lines of the mercury spectrum. With both the sources referred to above the apparatus remains steady within about 1 per cent. when the source is known to be fluctuating by at least 100 per cent.

* This is necessary in order that the total area of the two cross-sections, unobscured by the rotating disc, shall be constant; see also Dobson and Perfect, *loc. cit.*

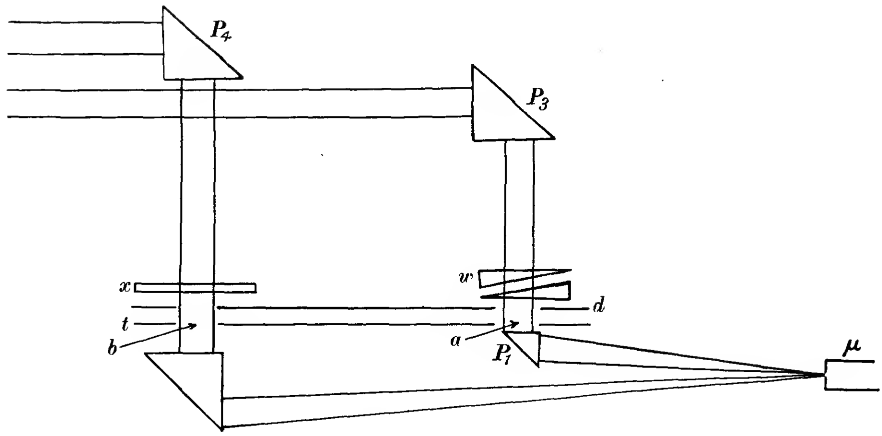

Fig. 9.

§ 8. CONCLUSION

At the present time three separate equipments—employing in detection the methods of timing the rate of drift, of balancing two cells, and of thermionic amplification—are assembled in this laboratory and are used in appropriate circumstances for measuring transmissions in the visible and the ultra-violet spectrum down to $0{\cdot}23\,\mu$. The intercomparison of results obtained by these methods and also with those obtained by a visual spectrophotometer is at present in progress and will give, it is hoped, valuable aid in the elimination of those systematic errors to which such measurements are so prone, and the detection of which from the internal evidence of any single method is so difficult.

In conclusion, I should like to acknowledge my indebtedness to my colleagues in the Optics Division for many suggestions, to Mr Turl for making the portable photometer shown in Fig. 2, to Mr Buxton of the Optics Workshop for invaluable help in the mechanical design of the equipment, to Mr F. M. Colebrook for the design of the amplifier and to Mr H. A. Thomas for assistance in developing the wireless technique.

A SPECTROPHOTOMETER FOR MEASURING THE AMOUNT OF OZONE IN THE UPPER ATMOSPHERE

By G. M. B. DOBSON, M.A., D.Sc., F.R.S.,
Boar's Hill, Oxford.

MS. received May 3, 1930. *Read June* 5, 1930.

ABSTRACT. The instrument consists essentially of a double spectrograph in combination with a photo-electric cell and a shutter and commutator. Two narrow bands in the sun's ultra-violet spectrum are isolated, their wave-lengths being chosen so that one of them is strongly absorbed by ozone and the other is but little absorbed. When the relative intensity of these bands is measured by the method described in another paper* it is possible to calculate the amount of ozone through which the light has passed.

The method described in another paper* has been applied to a spectrophotometer for measuring the amount of ozone in the upper atmosphere. For this purpose it is necessary to measure the relative intensity of two narrow bands in the sun's ultra-violet spectrum. The wave-lengths of these bands are chosen so that one of them is strongly absorbed by ozone while the other is but little absorbed. From the relative intensity of these two bands the amount of ozone through which the light has passed, can be calculated when certain constants of the instrument are known. As it is necessary to work very near the limit of the solar spectrum, the intensity of the radiation available is very small.

The general arrangement of the instrument is seen in Fig. 1. A double spectrograph is used, since the radiation in adjacent regions of the spectrum of longer wave-lengths is of enormously greater intensity and the small fraction of this radiation scattered by the lens and prism surfaces would produce a large error unless it were eliminated. The radiation passes into the instrument through a window W to the first slit S_1 and thence to the first dispersing system D_1. Three slits S_2, S_3, S_4 isolate three narrow bands about 10 Å wide (S_4 is for a subsidiary purpose which we will neglect here as this slit is normally closed). A lens L_1 near the slits ensures that all the light leaving the first dispersing system and passing through the slits reaches the second dispersing system D_2. As the focal plane is not at right angles to the beam, extra lenses L_2 and L_3 are inserted in the path of the longer wave-length so that it is brought to a focus at S_3. The dispersing system D_2 is similar to D_1 and recombines on the slit S_5 radiations of the proper wave-lengths which pass through S_2 and S_3. Scattered radiation of other wave-lengths which may pass S_2 and S_3 will be further dispersed and will not enter S_5. Two

* G. M. B. Dobson and D. S. Perfect, "A method of comparing very small amounts of light by means of a photo-electric cell and a valve amplifier," *Phys. and Opt. Soc. Discussion on Photo-electric Cells*, p. 79 (1930).

optical wedges w of neutral gelatine between quartz plates serve to reduce the intensity of the radiation passing S_3. Immediately behind S_5 is a sodium photo-electric cell C. A shutter disc d revolves close to S_2 and S_3, and admits the light from these alternately through the apertures a_2 and a_3. The shutter is shown in plan in Fig. 2. The extremities of the three pairs of apertures a_2, a_3, a_4 are portions of the same pair of mutually perpendicular diameters of the shutter disc. The

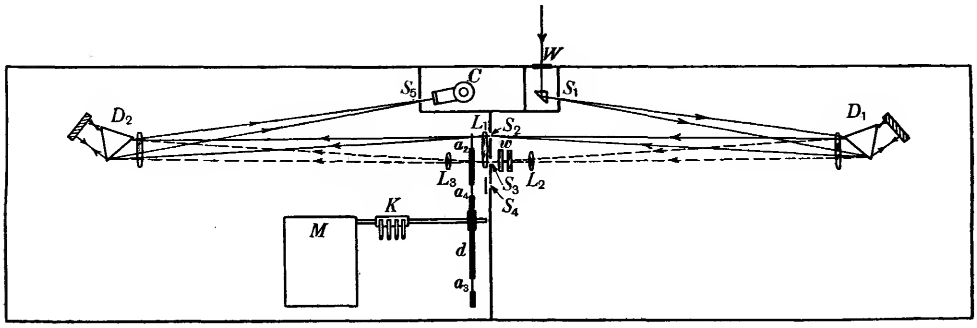

Fig. 1.

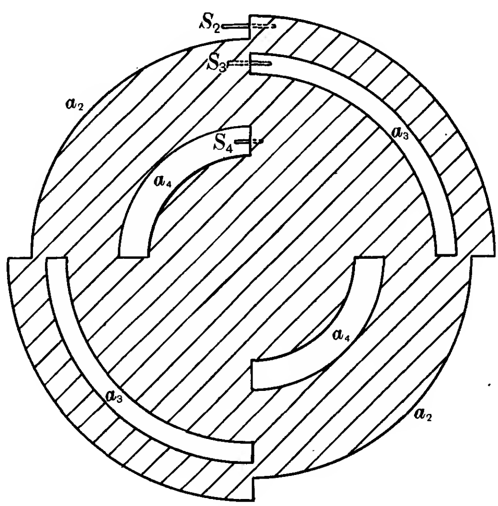

Fig. 2.

lengths of the corresponding slits S_2, S_3, S_4 are chosen so that their extremities lie on the same pair of planes passing through the axis of rotation of d (Fig. 1). The fulfilment of these geometrical conditions ensures that, if the energies passing through the two slits S_2, S_3 in unit time are equal, there will be no variation in the rate at which the total energy is received by the cell even when the shutter is rotating. The shaft of the shutter disc d (Fig. 1) also carries the commutator K and is driven by a gramophone motor M. The valve amplifier is contained in two boxes supported on antivibration packing, which are fixed on the other side of the instrument behind the spectrograph.

THE USE OF PHOTO-ELECTRIC CELLS IN BIOLOGICAL WORK

By V. E. SHELFORD,

Professor of Zoology, University of Illinois.

(Contribution from the Zoological Laboratories, No. 377.)

MS. received April 23, 1930. *Read June* 5, 1930.

ABSTRACT. As the flat surfaces commonly used to receive solar radiation are unlike the convex bodies of plants and animals, cells with sensitive surfaces in the form of spheres, cylinders, convex and concave hemispheres were tried. Cell form is best tested by continuous recording of sunlight with a potentiometer recorder.

The response of a double cylinder cell rose to 70 per cent. of its maximum within 30 min. after sunrise. The concave cell behaved more nearly like the double cylinder one. The apparent intensity rose to 80 per cent. of the maximum in $2\frac{1}{2}$ hours and a little later increased slightly to the maximum as the cylindrical cell did. Response increases very rapidly with the increase in surface exposed.

A double sphere cell followed the normal curve of intensity as calculated from air mass data for the wave-lengths to which it is most sensitive except that it showed an increase for a time when the sun's elevation was about 45°. The cell was mounted about 30 ft. above the ground and this increase was attributed to reflection from below.

While much work remains to be done, our most successful cell was a collapsed sphere cell with convex hemispherical sensitive surface. Its curve for the forenoon was most nearly comparable with the calculated intensities for the sun alone and showed a direct proportionality between intensity and current. A new design for this cell with accessories has been described elsewhere.

Ray filters should ordinarily be of glass. Plates of spherical curvature can be made from special glasses by the Corning Glass Company, Corning, N.Y., and ground to uniform thickness. Measuring circuits should be simple, such as unipivot instruments of several ranges so that the voltage of the batteries can be read on the same instrument as the cell current. The use of direct-reading instruments reduces the number of connexions to absorb moisture.

The terrestrial and shallow water outfit may include a vacuum cell to be used as a standard for the gas-filled cells. For use under water, clear vaseline was found to afford perfect insulation. Surface absorption varies greatly with cell form and screen colour. Peculiar optical properties of water with its suspended matter and transparency to different colours have been noted.

The information which should be available to purchasers of photo-electric cells is discussed, and a list of American makers of cells and accessories is given.

§ 1. RECEIVING SURFACES

A FLAT surface is commonly used to receive solar radiation for measurement. The bodies of plants and animals usually have convex surfaces. They frequently also present extensive surfaces to the sun when it is near the horizon. Accordingly, cells with several forms of sensitive surfaces were constructed by

Dr Kunz. Spherical forms, which appear ideal, and cylinders as well as convex and concave hemispheres were tried*.

Cell form is best tested by continuously recording sunlight. For this purpose the Leeds and Northrup motor-driven potentiometer recorder was used. It records for as many as sixteen cells at intervals of 10 min. or less depending upon the number. (The adjustment to zero is purely mechanical, depending upon the pinching of the deflected galvanometer pointer in a V-shaped moving slit.) This potentiometer is commonly made in a 10-millivolt range. The writer's latest plan to utilise various types of cells, vacuum and gas-filled, together with thermopiles with various types of exposure form is described elsewhere†. A direct current motor generator with voltage regulation is very much more satisfactory than batteries for the cell potential.

The findings of Kimball and Hand‡ with horizontal plane surfaces shows a comparatively close agreement (5 per cent.) between light as measured with an eye comparison instrument and total energy as measured with a pyroheliometer. This makes possible investigation of form effects with simple instruments such as black and white (electrical) resistance thermometers made from nickel or platinum wire wound on various forms. Recorders for these are also obtainable.

Some difficulties are involved in the measurement of sky effect. Since the sky is brightest near the sun, the difference (in cell form effect) between sun alone and sun and sky should not be large and could not be taken into account. However, some peculiar responses were suggested by blue- and violet-sensitive cells attributed to over-emphasis of the sky. Accordingly green- and yellow-sensitive cell and screen combinations should be used to form tests. Much work remains to be done in this field.

Cell forms

A spherical surface is probably correct for use among vegetation. Altogether nine cells were made by Dr J. Kunz with spherical sensitive surfaces. The sphere was a bulb-like expansion at the end of a tube half the sphere's diameter. This was enclosed in a larger tube of the same form. None showed a direct proportionality between current and sunlight intensity. All but one broke while out of use.

Cylindrical forms were also tried. These were test-tube shaped cylinders sensitised over their outside surfaces and enclosed in a similar outer cylinder. Two of these were made and neither showed direct proportionality between current and light intensity.

One collapsed sphere cell which showed a convex hemispherical sensitive surface gave a direct proportionality between current and intensity§.

* For figures showing cell forms see V. E. Shelford, *Laboratory and Field Ecology*, p. 335 (Baltimore: Williams and Wilkins Co.); V. E. Shelford and J. Kunz, "The use of photo-electric cells for light measurement in ecological work," *Ecology*, **10**, 298–311 (1929).

† V. E. Shelford, "Further notes on the acquisition and use of photo-electric cells," *Ecology* (April, 1930).

‡ H. H. Kimball and I. F. Hand, "Daylight illumination on horizontal, vertical and sloping surfaces, *U.S. Weather Bur. Monthly Weather Rev.* **50**, 615–28 (1922).

§ For the design of this cell and the accessories see J. Kunz and V. E. Shelford, *Rev. Scient. Instr.* **1**, 106–17 (1930).

The ordinary type of cell with a larger or smaller portion of the concave inner spherical surface sensitised was also used.

§ 2. RESPONSES OF DIFFERENT FORMS WITH CHANGES IN ANGLE OF INCIDENCE

The convex cell and double sphere cells were only about one-fifth as sensitive as the cylindrical and convex cells*. This accounts for their response beginning late in the morning. The curves were multiplied by a rather large factor to equalise the noon readings.

The double cylinder cells were tried only in a vertical position. (They failed while being remounted for use in a horizontal position.) The response of the double cylinder cell rose to 70 per cent. of its maximum within 30 min. after sunrise. The concave cell behaved more nearly like the double cylinder one. The apparent intensity rose to 80 per cent. of the maximum in $2\frac{1}{2}$ hours and a little later increased slightly to the maximum as the cylindrical cell did. This cell, while of a sensitivity equal to that of the cylindrical one, showed the first recordable response 20 min. later in the morning. The increase, however, did not represent the increase in intensity of general illumination but the increase in the amount of concave surface exposed to direct rays of the sun. Response increases very rapidly with the increase in surface exposed. The result is similar when a light is moved past the aperture in a circular path. The exposure of the sensitive surface of these concave cells begins when the sun is about 10° above the horizon and then increases up to 45–60°, depending on the aperture. The curves for concave cells always start rising later in the morning than those for a flat or convex surface of the same sensitivity and rise rapidly until the maximum amount of the surface is illuminated.

The double sphere cell followed the normal curve of intensity as calculated from air mass data for the wave-lengths to which it is most sensitive, except that it showed an increase for a time when the sun's elevation was about 45°. The cell was mounted about 30 ft. above the ground and this increase was attributed to reflection from below, a condition which is exaggerated under observatory conditions or on a roof. Such a location is, however, likely to be necessary to avoid shadows in localities where such apparatus can be set up with electric power and daily care available.

While much work remains to be done, our most successful cell was a collapsed sphere cell with convex hemispherical sensitive surface. Its curve for the forenoon is most nearly comparable with the calculated intensities for the sun alone, and it showed a direct proportionality between intensity and current. A new design for this cell with accessories has been described elsewhere†.

§ 3. COLOUR SENSITIVITY AND RAY FILTERS

Ray filters should ordinarily be of glass. Spherical globes of special glasses made to cover cells with spherical sensitive parts were tried but were not of uniform

* For figures showing the responses of cells of different forms, after correction to give apparent light intensity, all being reduced to the same noon maximum, see V. E. Shelford, *Laboratory and Field Ecology*; V. E. Shelford and J. Kunz, *Ecology*, **10**, 304 (1929).

† J. Kunz and V. E. Shelford, *Rev. Scient. Instr.* **1**, 106–17 (1930); see Fig. 1, p. 108.

thickness or quality. Rather large plates of spherical curvature can be made by the Corning Glass Company, Corning, N.Y., and ground to uniform thickness. These may be used to cover hemispherical cells, which is another advantage of this type.

§4. DESIRABLE FIELD MEASURING APPARATUS

For terrestrial and shore water work, measuring circuits should be simple, and a unipivot instrument of several ranges should be used so that the voltage of the batteries can be read on the same instrument as the cell current. Rawson instruments can be modified to do this, but the battery range must be made up by adding a series resistance which will stabilise the high voltage readings. The use of direct-reading instruments reduces the number of connexions to absorb moisture which, in the writer's experience, can give plenty of trouble, and usually, when such trouble occurs, it is under conditions which make it difficult or impossible to dry the apparatus.

*Portable apparatus for use in air**

To be read successfully with simple portable galvanometers under the ordinary conditions of light and shade, a cell should be large enough to give 250 microamperes at 125,000 metre-candles under 20 volts in order that 200 microamperes may actually be used in full sunlight (100,000 metre-candles). This is ideal, but cells which give 50 microamperes under the same conditions may be used in weak light by increasing the voltage. If a cell will give 0·05 microampere with 100 metre-candles under 20 volts, deep shadows may be read with an increase in voltage to 40 or 60 volts when the light is weak. It is unwise to carry batteries giving more than 100 volts; this means five 21·5-volt small B batteries which in themselves weigh 8 or 9 pounds. Even with great care, it will be difficult to keep the batteries and measuring circuit down to 15 pounds or less, and the entire equipment with filters, containers, and accessories below 40 pounds, which is sufficient to carry up a mountain.

The terrestrial and shallow water outfit may consist of only three or four large cells—one a vacuum cell, and two or three gas-filled cells, including at least one of potassium and one of rubidium. Caesium cells are as a rule not very sensitive, but good ones are very valuable for long wave-length work. A series of screens which may be put in place quickly, so as to give a set of readings very close together, is essential. (The time between such readings is decreased by the use of a well-damped direct-reading galvanometer.) The form and compactness of cells with hemispherical convex sensitive surface and screens can be greatly improved over that shown in Fig. 1, in the paper in the *Review of Scientific Instruments*, which was designed primarily for recording. The switch for controlling voltage can easily be greatly improved and reduced in weight, as compared with that which is used by the writer†.

* V. E. Shelford, *Ecology* (April, 1930).

† V. E. Shelford and J. Kunz, "The use of photo-electric cells of different alkali metals and color screens in the measurement of light penetration into water," *Trans. Wisconsin Acad. Science, Arts and Letters*, **22**, 283–98 (1926); V. E. Shelford, *Laboratory and Field Ecology*.

Problems connected with use of apparatus under water

(*a*) *Insulation.* Clear vaseline was found to afford perfect insulation and may be used to cover bare wires, to surround splices, etc., whereas all other substances tried failed. With a number of vaselined connexions and 50 metres of cable under water, the leakage was barely noticeable, being the same as with the apparatus on deck.

(*b*) *Surface effects.* As Poole and Atkins have suggested, the surface effects are increased to some degree by the effects of the spherical bulbs of the cells. A few readings with a cell with a spherical sensitive surface showed 14 per cent. just below the surface. Cells with concave surfaces showed 85 per cent. In general the centre of the spectrum appeared least affected by the surface. Certain glass filters appeared to have peculiar properties when used in connexion with concave cells. Surface effects should be studied with cells made between parallel glass plates.

(*c*) *Optical phenomena.* Peculiar optical properties of sea water (Puget Sound) with its suspended matter were noted. The maximum absorption of yellow and red is in the 2nd metre, green in the 4th and 5th, blue in the 7th and 8th. With increased plankton these maxima are all crowded together in the 2nd and 3rd metres. At 20 metres the water was most transparent to violet, least transparent to green and at 8 metres most transparent to yellow and least to blue. The optical properties of the water have been attributed chiefly to suspended matter, though dissolved matter is by no means out of the range of possibility.

§ 5. CONTINUOUS RECORDING UNDER WATER

It is desirable that continuous records be made both in the sea and in fresh water. The locality must be selected so as to avoid shore sediments which will affect the results. A 5-metre depth, rising and falling with the tide, is most desirable. The problem of fixing a carrying platform so as to present the cell to the sun at all hours and seasons, and protect it from wave action, is serious. In placing cells a thorough study of the sun's azimuths must be undertaken. Proper electrical insulation presents no particular difficulties.

§ 6. CELLS FOR TURNING ON LIGHTS*

For maintaining a given quality the problems are the same as for recording. Gas-filled cells used for turning on and off lights have decreased in sensitivity on long exposure to light under voltage. The voltage should be kept low, and preferably the circuit should be open at least four-fifths of the time. For accurate work the cells should be checked from time to time and adjustments made by small increases in voltage.

§ 7. PURCHASERS' DEMANDS

Purchasers should demand that a thorough study of each cell be made with reference to its individual properties which set limitations on the light intensity and voltage at which it may be used successfully. The ratings of the cell should allow

* J. Kunz and V. E. Shelford, "Turning on and off lights with the photo-electric cell," *Journ. Opt. Soc. Amer.* **12**, 693–6 (1926).

a margin of at least 25 per cent. for safety. It is essential to further progress that one or more cell makers develop a laboratory for the test enumerated below, and make possible the frequent checking of the cells used. The general specifications given below apply to both gas-filled and vacuum cells except where otherwise specified.

The demands should be as follows:

(*a*) The cell must bear a permanent number.

(*b*) The limits of direct proportionality between current and light intensity must be given (usually in terms of cell current).

(*c*) The voltage which can safely be used in full sunlight (100,000 metre-candles) and have the cell stable must be given for gas-filled cells. The minimum voltage that may be used with vacuum cells and the protecting resistance for gas-filled cells should be given.

(*d*) The limits of voltage and light intensity and cell current giving repeatable readings must be given for gas-filled cells.

(*e*) The ratings noted under (*c*) and (*d*) should be based upon tests in actual sunlight as well as in artificial light. A special sector disc for sun calibration has been described elsewhere*.

(*f*) The wave-length sensitivity curve including ultra-violet to 280 $m\mu$ should be required. Impurities in the metals or mixtures of metals give unusual curves. It is never safe to assume that a cell has the typical sensitivity of the metal from which it is supposed to be made†. This calibration is especially important; it requires more skill and technical and expensive equipment than any other requirement. It is absolutely essential to the estimation of the quality of light with screens‡.

(*g*) For foot-candle standards, cells should be screened or otherwise prepared so as to have essentially the sensitivity of the eye. Foot-candle measurement with a sodium cell may readily decrease 75 per cent., while those measured with the eye are not reduced more than 50 per cent.§

(*h*) The sensitive surface should be convex, giving correct readings for all light positions equivalent to those of the sun at the various hours and seasons. Preferably the cells should be insulatable for use under water.

§ 8. AMERICAN CELLS AND ACCESSORY MAKERS

G-M Laboratories, Inc., 1808 Grace St., Chicago, Illinois. Gas-filled cells. (See their Bulletin, p. 14.)

R.C. Burt Scientific Laboratories, 890–904 E. California St., Pasadena, California. Vacuum sodium cells only. (See their Bulletin, p. 271.)

* J. Kunz and V. E. Shelford, "Apparatus for testing photo-electric cells in sunlight," *Journ. Scient. Instr.* In Press.

† V. E. Shelford and J. Kunz, *Ecology*, **10**, 298–311 (1929); see Fig. 1.

‡ V. E. Shelford, "The penetration of light into Puget Sound waters as measured with gas-filled photo-electric cells and ray filters," *Pub. Puget Sound Biolog. Sta.* **7**, 151–68 (1929).

§ V. E. Shelford and J. Kunz, *Ecology*, **10**, 298–311 (1929); see Fig. 1 and compare with V. E. Shelford, *Laboratory and Field Ecology*, Fig. 133.

Case Research Laboratory, Inc., Auburn, New York. Vacuum strontium, barium, and possibly calcium, cells. (Cells cannot be supplied at present but will be available a little later.)

J. P. Foerst, University of Wisconsin, Madison, Wisconsin. Mendenhall thermopiles.

Rawson Electric Instrument Co., Cambridge, Mass. Unipivot meters.

Leeds and Northrup Co., 4901 Stenton Ave., Philadelphia, Pa. Potentiometer and resistance recorders for 1 to 16 points.

PHOTO-ELECTRIC PHOTOMETRY IN RELATION TO PHOTOTHERAPY

By HARRY D. GRIFFITH, B.A.,
Lecturer in Natural Philosophy, University of Aberdeen.

MS. received April 15, 1930. *Read June* 5, 1930.

ABSTRACT. A fully successful system for photometry of therapeutic lamps requires more knowledge of the physiological actions of light than is now available, but provisional solutions can be found. Consideration of the relation of response to wave-length for equal energies in a number of relevant cases, such as the action of light on proteins or on human skin, shows that the long-wave limit of sensitivity of the photometer should be about 313 mμ, but the best form for the response curve for shorter waves is difficult to choose. The selection of the erythema curve as found by Hausser and Vahle in 1921 as the sole basis is arbitrary and misleading if the re-determination of the curve (1928) is ignored. The author suggests a flat characteristic from 313 mμ to 250 mμ for the response curve of the photometer as the best compromise. Cadmium photo-electric cells are widely used because of the appropriate position of the threshold wave-length, either with bare quartz windows or with a screen of uviol or vita glass; the former are too sensitive to the shorter waves, the latter too insensitive. Either gives a practically useful means of studying the change of biological activity of any one type of source with age or running conditions. Neither is fully satisfactory for comparing sources of different types (e.g. a carbon with a mercury arc) but such comparison is probably meaningless since the physiological responses to the lamps are different in kind and cannot be approximated by any system of control of dosage.

§ 1. DEPENDENCE OF SOME ACTIONS OF LIGHT ON WAVE-LENGTH

In attempting to develop a method for the photometry of therapeutic lamps a fundamental problem is encountered when the relative biological importance of the different wave-lengths present in the spectrum of the source has to be assessed. The following factors call for consideration in this connexion because in these cases experimental investigation of the relative activity of individual wave-lengths has been possible.

Exposure of many proteins to ultra-violet light causes photo-chemical change in them which may be followed by flocculation*. The precipitation of albumin has been investigated using monochromatic light, and greatest sensitivity was found about 260 mμ; for equal incident energy, the rapidity of the reaction was found to be related to wave-length as shown in Fig. 1, curve (*B*). The lethal action of light on bacteria is probably intimately related to this action on the protein of the cell contents, and therefore has a similar relation to wave-length. The bactericidal action of light is illustrated in Fig. 2, which shows the effect of the mercury spectrum, formed on an agar surface which had been spread with an emulsion of Staphylococci

* Burge, *Amer. Journ. Physiol.* **36**, 21 (1915); Sonne, *Strahlentherapie*, **28**, 50 (1928).

previously. After incubation, colonies failed to develop where certain spectral lines had fallen, showing that the bactericidal action starts about 300 mμ and extends to the limit of the mercury spectrum. Quantitative study of this effect gives results as in curve (*A*) of Fig. 1*. For the case of the action of light on Paramecium, the curve takes the form (*C*), the slightly decreased activity of the shortest wave-lengths being probably due to failure to penetrate far enough into the cell.

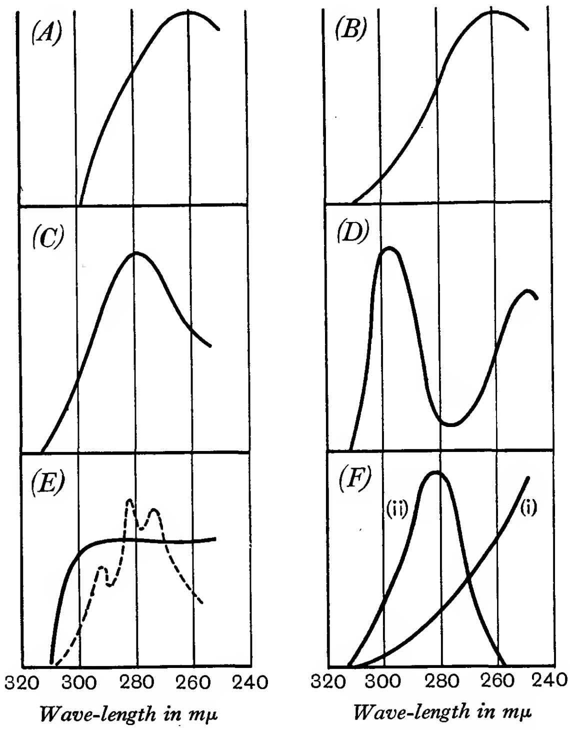

Fig. 1. Dependence of some actions of light on wave-length.

(*A*) Bactericidal action.
(*C*) Killing of Paramecium.
(*E*) Action on ergosterol (dotted curve gives absorption coefficient).

(*B*) Flocculation of protein.
(*D*) Erythema of skin.
(*F*) Sensitivity of cadmium cells.
(i) Unscreened.
(ii) Screened with 1·5 mm. uviol glass.

Another of the physiological actions of light which is amenable to quantitative investigation is the action on human skin. When ultra-violet light is incident on the skin there is no reaction until the end of a "latent period" of 2 to 6 hours after exposure; then a reddening of the skin (erythema) develops at the site of irradiation. The production of erythema by monochromatic light, using the same energy at different wave-lengths, was investigated by Hausser and Vahle† in 1921 and again by Hausser and Schlechter‡ in 1928 with results shown in Fig. 1 (*D*). The occur-

* Gates, *Journ. Gen. Physiol.* **13**, 240 (1929); Lassen, *Strahlentherapie*, **27**, 761 (1928).
† Hausser and Vahle, *Strahlentherapie*, **13**, 41 (1921).
‡ Hausser and Schlechter, *Strahlentherapie*, **28**, 25 (1928).

rence of the second maximum in the curve about 250 mμ, which was not found in the earlier experiments, is important and brings the production of erythema more closely into line with the other biological actions of light. Unfortunately there has been a tendency to give undue weight to the earlier, incorrect, curve and to take it as the sole criterion for assessing the relative therapeutic importance of different wave-lengths. The older curve is seen to give too little weight to waves shorter than 280 mμ. Recent work on the intensity of the pigmentation which follows erythema has been published* showing that the wave-lengths of the second maximum are twice as effective as are those of the first.

The last of the effects of light to be considered is the photo-synthesis of vitamin D from ergosterol. This action is known to start at 302 mμ in the spectrum, but there has been considerable discussion as to how far on the short-wave side of this limit the active band extends. Kon, Daniels, and Steenbock† have shown that a series

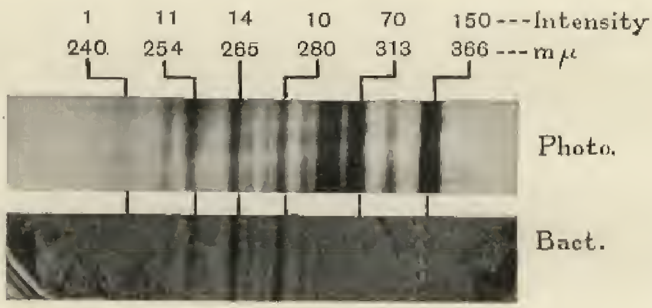

Fig. 2. Bactericidal effect of mercury spectrum. Upper spectrum recorded on Velox, lower spectrum by bactericidal action.

of monochromatic wave-lengths between 300 mμ and 254 mμ are all equally active per erg absorbed in causing this photosynthesis. This result is represented by the full line in Fig. 1 (E); the broken line gives the extinction coefficient of ergosterol. The fuller study of the action of light on ergosterol‡ has given no reason to doubt this result when moderate ultra-violet intensities are involved, of the order used in phototherapy. When intensive radiation close to a powerful source is employed, other factors enter which complicate the process of Vitamin formation.

It has been said that radiation shorter than 280 mμ cannot be of therapeutic importance because it is so completely absorbed in the horny layer of the epidermis and cannot penetrate to the living cells below. However it has been shown that vitamin D can be absorbed into the blood stream if applied to the skin surface§; similarly, the production of erythema by short waves could be explained by the diffusion into deeper layers of a product of a photochemical change occurring at the surface. Nothing is known of the precise range of wave-lengths which are of value in the treatment of surgical tuberculosis by light.

* Uhlmann, *Strahlentherapie*, 35, 361 (1930).

† Kon, Daniels, and Steenbock, *Journ. Amer. Chem. Soc.* 50, 2573 (1928).

‡ Reerink and Van Wijk, *Biochem. Journ.* 23, 1306 (1929).

§ Hume, Lucas, and Smith, *Biochem. Journ.* 21, 362 (1927).

§ 2. COMPARISON OF SOURCES

Summarising these facts, we may definitely conclude that in estimating the probable physiological activity of a light-source only radiation shorter than 313 mμ should be taken into account; to decide on the probable run of the curve of physiological response to shorter waves is a far more difficult matter. In practice, two main types of problem arise; the comparison of sources of similar spectral energy distribution so that the effect of age or over-voltage may be allowed for, and the comparison of sources which have very different spectra. Strictly the two

Table 1. Relation of bactericidal power of sources to photo-electric power

Source	Watts	Photo-electric power	Bactericidal power
Carbon arc	4500	550	690
„ „	700	15	18
Tungsten „	364	62	55
„ „	175	20	23
Mercury „	291	40	34
Iron „	400	22	26

Table 2. Relation of erythema produced to photo-electric power
Carbon arcs with a variety of cores used

Core	Watts	Photo-electric power	Degree of erythema
Pulverised iron	2000	10	10
Cerium C	2340	9·4	7·5
Plain carbon	2320	10	7·5
Cerium A	2200	8·1	5
Cerium B	1900	6·5	5

cases are not really separable for, as is well known, the spectra of arc lamps do change when the running conditions are changed. However, the second problem is not pressing, for no experienced clinician expects to get exactly similar results, even as regards skin reaction, with carbon and with mercury arcs, however the times of exposure are proportioned. The recent work of Hausser and Schlechter has given one reason for this.

Photo-electric methods have been applied by several workers with success to the first problem, and with partial success to the second. The photo-cathode which has been generally employed is cadmium, which has a threshold at 313 mμ, but recently the use of uranium and of lithium has been reported*. Cadmium cells in bulbs of uviol glass partially transparent to the ultra-violet were applied by Dorno† to the study of the short-wave components of solar radiation. When the use of arc lamps became general for phototherapy about 1925 and a rapid method for estimating their probable value became necessary, it seemed that cells of Dorno's type

* Rentschler, *Brit. Journ. Actinotherapy*, **4**, 201; **5**, 14 (1930)
† Dorno, *Phys. Z.* **18**, 381 (1917).

would not give due weight to the short wave-length radiation given by these sources, since the bulb has small transmitting power below 280 mμ. With the help of colleagues on the medical staff the author* therefore tried cadmium cells with quartz windows and found that such cells could be made to give response to a series of electric arcs of different types in satisfactory agreement with the bactericidal action of the lamps, and fair agreement with the erythema produced. Some results are given in Table 1. Angus†, working with one of our cells at the National Institute for Medical Research, gives results for the production of erythema by arcs burning various varieties of cored carbons as in Table 2. The concordance between the response of the photo-electric cell and the response of the skin seems to us to be fair, except for the single case of the plain carbons which are given undue weight by the cell. Angus found that good agreement could be obtained in all these cases by the use of a filter of 1·58 mm. of vita glass placed over the quartz window of the cell, though this addition excludes too much of the shorter radiation.

§ 3. TYPES OF PHOTO-ELECTRIC CELL USED

Fig. 3 shows some cells used by us at various times. In type *A* the cadmium cathode is scraped clean immediately before the cell is sealed off. In *B*, cadmium is distilled on to the cathode from the side tube. Cell *C* is designed to take in radiation

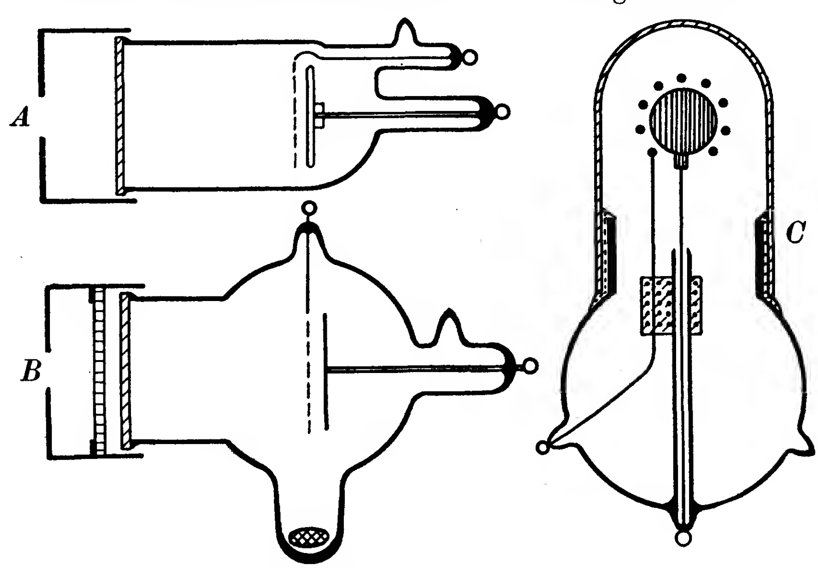

Fig. 3. Cadmium photo-electric cells.

from the whole sky, instead of from a point source only. A simple gold-leaf electroscope with scale and eyepiece has served us best as recording instrument, since it can be charged conveniently by friction and is then entirely self-contained. Our usual practice has been to set up the cell, which is carried by the stand of the electroscope 10 ft. from the lamp, and then to time the fall of the leaf through a standard

* Griffith and Taylor, *Journ. Hygiene*, **25**, 218 (1926).

† Angus, *Brit. Journ. Actinotherapy*, **2**, 17 (1927).

voltage-drop. The results are computed to give the "ultra-violet power" of the lamp in arbitrary units analogous to candle-power for visible light. Used in this way, fatigue and dark current give no trouble within the accuracy aimed at. The physical characteristics of such cells are illustrated in Fig. 1 (*F*). By the use of the uviol or vita glass filter, the cell can be made to have a response curve close to that of the first loop of the erythema curve, but the combination of cell and filter is then too insensitive to the shorter wave-lengths. The ideal solution would probably be to fit a filter which would flatten out the response curve to the form of the full line in Fig. 1 (*E*), but we have not succeeded in finding a material with suitable absorption characteristics which are permanent. In any case, it would seem preferable to use cells with quartz windows, and fit outside filters if required, as in Fig. 3 (*B*). If the cell bulb is blown from uviol glass, as is the German practice, it must be difficult to secure uniform thickness and transmission. However, such cells are widely and successfully employed on the Continent and have been reported on by numerous workers since their first application by Dannmeyer to artificial light-sources in 1926*.

Direct reading instruments, involving the use of amplifying valves, have been designed by several workers† for use in conjunction with cadmium cells. The "ticking" electroscope is also convenient and gives a simple means of integrating readings over a period of time by automatic recording of the beats of the leaf. The method of the neon flasher described by Poole‡ is inapplicable because the currents flowing in the cadmium cell are much smaller than those given by sodium or potassium cells. The method recently devised by Rentschler§ and referred to above seems to offer an ingenious solution to the problem of integration.

The cadmium cell has proved of value in several directions. Firstly, the well-known deterioration of mercury arc lamps with age is extremely hard to allow for in a big hospital unless some means for direct measurement of the ultra-violet radiation is available. Dosage can be controlled in this case and weak lamps detected very readily and quickly by the cell. If lamps of new type are installed, cell readings taken in conjunction with a spectrum photograph give indications as to what results may be expected from them. If comparison of very dissimilar sources is attempted, one of which is rich in short waves as shown by the spectrograph, a lightly screened cell, with response curve similar to (*F*) (ii) of Fig. 1 will give better agreement with erythema than an unscreened cell; but where there is great difference in spectra, similar clinical results are not to be looked for, however dosage is adjusted. Most useful results could be obtained as to the intensity and distribution of the short ultra-violet rays present in daylight indoors or outdoors by cells of the type *C* of Fig. 3, which are adapted to take in radiation from all angles. Rapid measurements can be made of the capacity of materials to transmit the biologically active components of sunlight‖. Where a steady source of light is required with spectral

* Dannmeyer, *Strahlentherapie*, **22**, 738 (1926); Ruttenauer, *ibid.* **27**, 794 (1928); Büttner, *ibid.* **32**, 404 (1929).

† Harris, *Journ. Scient. Instr.* **6**, 1 (1929); Pohle, *Amer. Journ. Roentgenology*, **20**, 338 (1928).

‡ Poole, *Scient. Proc. Roy. Dublin Soc.* **19**, 17 (1929).

§ Rentschler, *loc. cit.*

‖ Suhrmann, *Strahlentherapie*, **31**, 396 (1929).

composition approximately similar to sunlight in the ultra-violet, filament lamps in bulbs of glass transparent to the ultra-violet are most convenient. They are also excellent for absorption spectroscopy as far as 265 mμ. In the study of sunlight or of these filament lamps it is necessary to pay close attention to the form of the sensitivity curve of the cell on the long wave side since the intensity of the radiation of these sources increases so rapidly with wave-length. Sodium cells in glass, for instance, which give maximum response at 362 mμ, could not give results related to any of the known biological actions of light.

It would seem that complete success in the development of a system of therapeutic photometry must depend upon the working out of further curves such as those of Fig. 1, so that we may know more definitely what wave-lengths are appropriate for attainment of the clinical result desired. It is certain that the physiological action of light is much more variable with wave-length than in the case of X-rays, and, as in the latter case, it must be recognised that some specification of quality as well as of quantity is essential for a correct statement of dosage. Meanwhile, the cadmium cell, with its threshold of sensitivity so well in accord with the curves of Fig. 1, is the most promising measuring instrument. If control of dosage by erythema is intended, slight screening of the cell may be desirable; if the general light-sensitivity of proteins is taken as fundamental, the unscreened cell is more suitable.

SELENIUM CELLS AND THEIR USE IN SOUND FILM REPRODUCTION

By Dr H. THIRRING,
Professor of Physics in the University of Vienna.

MS. received June 13, 1930. *Read June* 4, 1930.

ABSTRACT. The disadvantages of the selenium cell are discussed, and reasons are given why these do not interfere with the use of the cell for sound film reproduction. It is claimed that the quality of sound reproduction by means of selenium cells is equivalent to, if not better than, that obtained with the best alkali photo-electric cells.

§ 1. INTRODUCTION

It has been widely assumed that selenium cells are not suitable for the reproduction of talking picture films on account of the time-lag in their response to light. The majority of inventors who have constructed reproducing equipments have, therefore, used alkali photo-electric cells. On the other hand, some companies have preferred selenium cells from the beginning and have adapted their equipments for use with them. They seem to have been quite successful, as may be concluded from the rapidly increasing demand for selenium cells in sound film work.

§ 2. DISADVANTAGES OF SELENIUM CELL

It may be not uninteresting, therefore, to discuss the question why the selenium cells, in spite of their undeniable drawbacks, may be preferred to the theoretically more satisfactory alkali cells. The disadvantages of the selenium cells may best be illustrated by the diagram given in Fig. 1 showing the photo-electric current as a function of time in a cell which is supposed to be kept at constant illumination during the interval from t_1 to t_2, and is kept in the dark before t_1 and after t_2. The diagram shows in a somewhat exaggerated way all the disadvantages of the selenium cell:

(1) The dark current is not perfectly constant but varies slowly, the change of resistance being due to changes of temperature, polarisation, and other causes.

(2) The action of the illumination does not take place instantaneously. The current rises rapidly at first, then more slowly and reaches its final value only after a few seconds. This time-lag is still greater at the change from light to darkness. After a prolonged illumination with a strong source of light, say, for instance, sunlight, the cell will recover its initial dark resistance only after a few hours. This inequality of the time-lag causes an unsymmetrical distortion of the current-time curve.

(3) There is a fatigue phenomenon. When the cell is exposed to a constant illumination the current, after reaching its peak value, will diminish gradually.

The first and third mentioned properties of selenium, viz. the inconstancy of dark current and the fatigue, are rather serious obstacles in the way of using selenium cells for photometric work; they do not interfere, however, with their use in sound

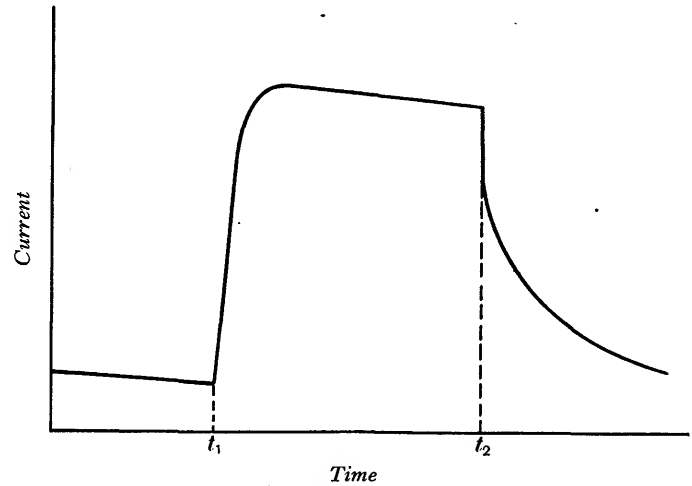

Fig. 1. Curve showing time-lag in the action of light on a selenium cell.

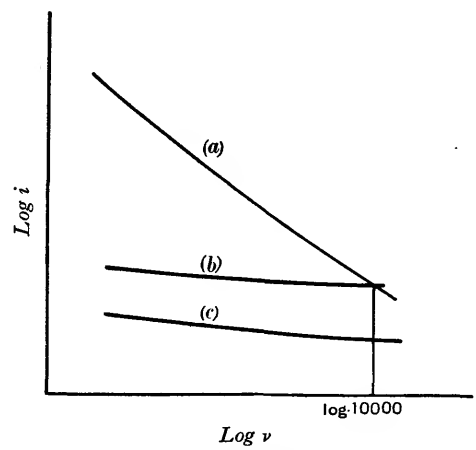

Fig. 2. Response-frequency curves. (*a*) Selenium cell not compensated; (*b*) Selenium cell compensated; (*c*) Gas-filled alkali cell.

film reproduction. A serious objection, however, seems to arise from the inertia of the selenium which causes a distortion of speech and music by weakening the higher frequencies. A distortion of that kind may, however, be easily compensated, provided that the response-frequency curve is smooth enough. Most fortunately this is the case with the selenium cells. Fig. 2 shows a diagram in which the logarithms of the current amplitudes caused by intermittent illumination are plotted against the logarithms of the frequency. The response-frequency curve of

the author's selenium cells is given by curve (*a*) which is very nearly a straight line, the angle of inclination showing that the current amplitudes are approximately inversely proportional to the frequency. Hence the frequency distortion caused by the selenium may be easily compensated by a capacitive resistance. The cells are usually connected to the amplifier by means of a resistance-capacity coupling. When the capacity of the coupling condenser is suitably chosen, for instance as low as 200 cm., the frequency distortion is fully compensated. Expressed in terms of our diagram, proper compensation is effected by rotation of the response-frequency curve about the region of higher frequencies. The compensated response-frequency curve of the selenium is given by the line (*b*) in Fig. 2. When we therefore want to compare what we may call "the photophonic efficiency" of selenium cells with that of alkali cells we have to measure the response of both types of cells in the region of the highest audible frequencies. If it should turn out, for instance, that the response-frequency curve of a certain photo-electric cell intersects that of the selenium cell at a frequency of, say, 7000 cycles, we should regard the former cell as being more efficient than the selenium cell because the compensated curve of the latter would lie below that of the former. These comparative measurements have to be made, of course, with equal light energy flux, that is to say, with equal number of *lumens* and not with equal light *intensity* on both cells, for in the reproduction of talking films there is a given flux of light passing through a virtual narrow slit on the sound track. This given flux, which is of the order of magnitude of approximately 1/10 of a Hefner lumen, has to be thrown on either cell and has to be more condensed in the case of selenium cells with a very small light-sensitive surface.

§ 3. COMPARISON OF SELENIUM AND PHOTO-ELECTRIC CELLS

I have made a number of comparative tests between selenium cells of the so-called condenser type which are made according to my patents by the Selenophon Co., Ltd., in Vienna*, and all the alkali photo-electric cells which I could get hold of—including several commercial cells used in talking film equipments. The response-frequency curve of an average good gas-filled alkali cell is given by (*c*) in Fig. 2. If there exists an intersecting point at all between the response curves of selenium and the alkali cells I tested, it seems to lie appreciably beyond a frequency of 12,000 cycles. Up to that frequency the current output of the selenium cell at a given light flux is markedly higher than that of the alkali cells. I am glad to have the opportunity of meeting here the leading men in photo-electric work, and I should like to take the opportunity of inviting the inventors and makers of alkali photo-electric cells to compare the photophonic efficiency of their cells with that of the selenium cells of the condenser type by means of a testing device which has been set up for that purpose in the demonstration room. All my previous experience in this field has been unfavourable as regards the efficiency of the alkali cell; they always seemed to be "indisposed" or had suffered from having been overloaded previously.

The obvious advantage of the selenium cells lies in the fact that their response

* A short description of these cells has been given in *Proc. Phys. Soc.* **39**, 97 (1926).

to modulated light of a given number of lumens is even in the region of the highest acoustic frequencies stronger than that of the alkali cells. Hence less amplification is necessary and less distortion of music and speech may arise from reaction or from the almost inevitable electric and magnetic effects induced by the mains and the projecting machine. In other words, the current output from the selenium cell lies more safely above the general disturbance level than that of the alkali cells.

Another objection which has frequently been raised against the use of selenium cells in photophonic work is based on the fact that the current flowing through the cell at a given voltage is not a linear function of the light intensity. In Fig. 3 the electric current in a selenium cell is plotted against the amount of light falling on the cell. The curve (*a*) represents the results of measurements of the kind which has usually been taken in connexion with selenium cells, viz. "static" measurements with an illumination which is kept constant during each reading.

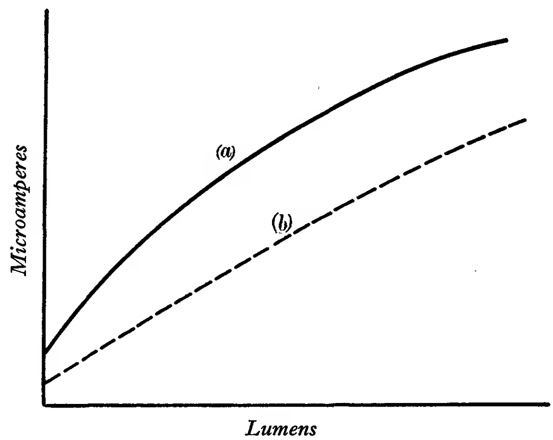

Fig. 3. Current as function of light falling on cell. (*a*) Direct current caused by continuous illumination; (*b*) Alternating current caused by intermittent illumination.

From the non-linearity of curve (*a*), Fig. 3, and also from the asymmetry of the time-lag as represented in Fig. 1, it has been theoretically concluded that in addition to the frequency distortion there would also be an amplitude distortion which would give rise to new harmonics, that is to say, to false overtones. Although this prediction seems to be theoretically quite correct, it has not been checked by experience. On the contrary, the quality of sound reproduction by means of selenium cells is equivalent to, if not better than, that obtained with the best alkali photoelectric cells. The reason for this apparent discrepancy between theory and experiment seems to lie in the fact that from measurements taken with constant or with slowly varying illumination no conclusions must be drawn about the behaviour of the cells with illuminations of audible frequencies.

From the large amount of time-lag as represented in the "static" current-time curve shown in Fig. 1 a considerably smaller response to frequencies of 10,000 cycles might have been expected than that which has actually been measured with intermittent light. The fact is that static measurements cannot give us that portion

of the curve which lies within a fraction of a second after t_1 and t_2. It may, however, be inversely concluded from the actual amount of response to high frequencies that the limit of the angle between the tangent to the curve and the ordinate is very small at the points t_1 and t_2. There are further reasons to assume that the limits of the angles are *equal* at these two points. The asymmetry of time-lag disappears, therefore, in the case of audible frequencies.

In a similar way the conclusions concerning the amplitude distortion drawn from curve (*a*) in Fig. 3 are erroneous. The point in question is not the value of the *direct current* caused by continuous illumination but the *alternating current* caused by intermittent illumination. In the latter case the amplitude of current varies nearly linearly with the amplitude of light, as shown by the broken line (*b*) in Fig. 3. That is the reason why, contrary to the above-mentioned theoretical predictions, no noticeable amplitude distortion occurs in sound film reproduction with selenium cells.

Summing up, I may assert, therefore, that the doubt cast on the use of the selenium cells on account of their inertia has been a prejudice caused by incorrect conclusions drawn from D.C. measurements with continuous illumination. Experience drawn from a great number of talking film reproducing apparatus equipped with selenium cells of the condenser type has shown that these cells are very efficient instruments for this purpose when connected by a suitable capacity-resistance coupling to the amplifiers. It may be added in this connexion that the best results have been obtained by using cells possessing a light-sensitive area of only a few square millimetres upon which the light passing through the sound track is focussed by a suitable optical system.

THE MANUFACTURE OF SELENIUM CELLS

By Major C. E. S. PHILLIPS, O.B.E., F.Inst.P.

MS. received April 15, 1930. *Read June* 4, 1930.

ABSTRACT. The paper contains a brief description of several methods of making selenium cells, together with a comparison of their relative merits. The effect of oil in reducing "lag" is pointed out. Sublimation *in vacuo* is referred to and attention called to the desirability of avoiding the formation of selenious acid in all cases where the cells are made at atmospheric pressure; a method is suggested whereby this may be accomplished.

SELENIUM cells or bridges are usually prepared by smearing molten selenium upon an insulating base which carries a suitably conducting grid*. The vitreous layer so obtained is then cooled and reheated so as to convert it to a grey crystalline light-sensitive allotropic form. There is also another method—sublimation. The former is almost universally adopted now-a-days but suffers from the defect that the thickness of the selenium layer is difficult to control. On the other hand, the tendency of the selenium to oxidise is not excessive and cells so made do not easily break down. Owing however to the high surface tension of molten selenium when in contact with glass, slate, porcelain, or other suitable insulators which form the base of the grid, it requires considerable experience to master the technique of cell-making on this plan.

With a view to devising a means whereby selenium cells can be made in such a way as to ensure uniformity and reliability the writer has attempted to develop the method in which selenium vapour is condensed upon a glass plate carrying a suitable platinum grid. The hot vapour, however, oxidises somewhat in air at ordinary pressure, and although very sensitive cells may be quickly made in this way they frequently break down when a P.D. of say 60 volts is maintained across them for some hours continuously. This is due to the formation of the oxide already referred to, which changes to selenious acid and absorbs moisture on cooling. Cells that break down from this cause do so owing to electrolysis, the selenium near the positive contact becoming dissolved by the acid accumulating there. The first indication of trouble is the unsteady deflection of the microammeter needle or crackling sound from a telephone in the circuit. For occasional use however, when the P.D. of 30 to 60 volts is not applied for more than a minute without a rest, cells made by this process frequently last for many months before failing. The writer has noticed that a great increase of resistance may be produced in such cells by a puff of tobacco smoke impinging upon them. This curious result was traced to the action of small quantities of oil vapour, and it was soon found possible to increase the resistance of the cells 100 per cent. or more by merely spraying or painting them

* This general description is also intended to cover the preparation of cells of the "condenser" type.

when hot with oil of cloves. In this way the resistance could be increased without any serious diminution of the light-sensitivity, and a cell that showed a "dark current" of 200 microamperes for a P.D. of 15 volts was usually changed by oiling, so that with a P.D. of 60 volts no current was indicated although a light of 40 candle-feet produced a deflection of from 500 to 1000 microamperes. It is noteworthy too that in such cases the deflection fell to practically zero, with negligible lag, when the light was extinguished.

Reversal of the direction of the current usually gave rise to a marked difference of resistance due to polarisation. When a cell was plunged while hot into pure vaseline this effect was less noticeable, but in no case, irrespective of the method of manufacture, has a cell appeared to be quite free from this defect. The more or less gradual rise of current in selenium cells after the first maximum deflection is reached appears to be due to slightly increased conductivity brought about by the formation of acid at the positive electrode. It may be said generally that if the resistance of a selenium cell remains constant for some minutes, before slowly increasing due to rise of temperature or the formation of gas at the electrodes, it is usually because of a balance of conditions. Sublimation *in vacuo* might be taken advantage of to avoid oxidation, but experiments have shown that under such conditions the vapour comes off freely from the grey form of selenium, and that the grid becomes heavily coated before it has had time to reach a temperature by radiation high enough to produce a layer of suitable crystals over its surface. Possibly an elaborate apparatus could be devised to overcome this drawback, but in view of the far simpler plan of sublimation in, say, an atmosphere of an inert gas it does not seem worth while.

The deposition *in vacuo* of a vitreous layer of selenium thrown off by means of an electric discharge from a cathode coated with the grey variety and consequently crystallised may be another solution of the problem. The chief difficulty to be met with in that case would be the shrinkage of the vitreous coating, and the formation of innumerable pinholes in it as the crystallisation temperature is gradually reached.

The writer is engaged upon the problem of depositing pure crystalline selenium upon heat-resisting glass carrying a platinum grid, the whole being kept in an atmosphere of dry CO_2. If that plan succeeds and a cell so made and hermetically sealed shows no sign of polarisation, there will only remain the change of resistance due to a slight rise of temperature to be coped with, and a method for automatically compensating for this has already been devised by Messrs Engelke and Read.

It may therefore become possible, after all, to make use of the selenium cell in quantitative work.

INFRA-RED SENSITIVE CELLS

By Dr FRITZ SCHRÖTER and Dr FRITZ MICHELSSEN.

(Communication from the Laboratory of the Telefunken-Gesellschaft für drahtlose Telegraphie m.b.H., Berlin.)

MS. received May 31, 1930. *Read June* 4, 1930.

ABSTRACT. The paper describes the method of preparing selenium-tellurium cells and thallium sulphide cells which are sensitive to the infra-red region of the spectrum. Curves are given showing the variation of sensitiveness of the different types of cell with wave-length. The application of such cells to telegraphy and telephony by means of bundles of invisible rays is discussed.

§ 1. INTRODUCTION

THE use of beams of infra-red rays to carry telegraphic signs or speech necessitates a detecting cell which reproduces the modulation frequency of the ray. In telephony vibrations up to at least 2000 cycles per second have to be received and amplified in this manner. Nothing but the photo-electric effect, therefore, comes into consideration.

Elster and Geitel photo-electric cells lose the infra-red sensitiveness, which is obtainable first of all, too quickly for them to be of any importance for the problem in hand. We therefore worked on the already observed and utilised infra-red sensitiveness of ordinary selenium cells. As, however, this property cannot in general be reproduced with pure selenium, we tried the addition of tellurium, this being suggested by considerations of atomic physics relative to the ionisation potential. In the periodic system tellurium is the element with the next higher atomic weight in the selenium group. As the measurements given in the table below indicate, the addition of about 10 to 13 atomic per cent. of tellurium causes a decided and reproducible shift of the spectral sensitiveness of selenium towards the infra-red. As, however, the dark resistance of the selenium-tellurium alloy decreases very much as the content of tellurium increases, the desired absolute values of the infra-red sensitiveness can only be reached if extremely thin layers of the substance are used, whose thickness approximately equals the depth of penetration of the incident radiation. In this way one avoids the alteration in conductivity caused in the surface layer being masked by the effect of under-layers having a comparatively small dark resistance.

§ 2. MEASUREMENT OF EXPERIMENTAL CELLS

To avoid the tedious measurement of all the experimental cells by means of a spectrum, the following filters were used to limit the wave-lengths:

Wratten infra-red filter No. 87, transmitting $\lambda > 0{\cdot}745\mu$;

Schott's "Rotglas" R.G. 5, transmitting $\lambda > 0{\cdot}675\mu$.

Since in ordinary selenium cells the greatest sensitiveness lies at $0{\cdot}7\mu$ (see Fig. 2) it was possible to determine by difference the percentage share in producing alteration of resistance due to the three spectral regions

$$\lambda < 0{\cdot}675\mu;\ 0{\cdot}675\mu < \lambda < 0{\cdot}745\mu;\ \text{and}\ \lambda > 0{\cdot}745\mu,$$

relative to that of the unfiltered radiation. In the result so obtained the quadratic relation between light intensity and alteration in conductivity is, it must be admitted, inaccurate, and this inaccuracy could be avoided by measurement of the spectral distribution of sensitiveness (see Fig. 2) by means of a lamp adjusted to constant energy at all wave-lengths. Nevertheless, the results obtained with filters (see table) plainly show a shift of the sensitiveness towards the infra-red as the tellurium content increases, while it must be noted that with thinly-coated cells of pure selenium (e.g. such as are obtained by cathodic sputtering) the maximum sensitiveness lies at shorter wave-lengths than in the case of ordinary selenium cells.

Table

Percentage alteration of resistance in three spectral intervals (alteration of resistance due to unfiltered radiation = 100 per cent.)

Make	$\lambda < 0{\cdot}675\mu$	$0{\cdot}675\mu < \lambda < 0{\cdot}745\mu$	$\lambda > 0{\cdot}745\mu$	Remarks
v. Bronk No. 7882	32	60	8	Standard selenium cell
Gripenberg	16	68	16	,, ,,
Thirring No. 1184	13	63	24	,, ,,
Television Supplies, Ltd.	22	62	16	Thinly-coated selenium cell (vaporisation)
Gripenberg Rot I	62	29	9	Thinly-coated selenium cell (cathodic sputtering)
Gripenberg Rot II	78	18	4	,, ,,
7 atomic per cent. tellurium added, No. 2	37	35	28	Thinly-coated selenium-tellurium cell
7 atomic per cent. tellurium added, No. 1	40	27	33	,, ,,
10 atomic per cent. tellurium added, No. 2	40	19	41	,, ,,
10 atomic per cent. tellurium added, No. 27	38	16	46	,, ,,
13·6 atomic per cent. tellurium added, No. 49	36	17	47	,, ,,
13·6 atomic per cent. tellurium added, No. 51	32	15	53	,, ,,
13·6 atomic per cent. tellurium added, No. 70	41	11	48	,, ,,
13·6 atomic per cent. tellurium added, No. 71	36	18	46	,, ,,
13·6 atomic per cent. tellurium added, No. 73	37	10	53	,, ,,

The amount of selenium added, shown in the first column of the table, relates to the selenium-tellurium alloy used as the starting product in the process of sputtering. The reason for the variations noted in its influence is perhaps to be found in alterations of concentration on the surface of the cathode as a result of the sputtering.

§ 3. METHOD OF MANUFACTURE OF SELENIUM-TELLURIUM CELLS

We prepare the cells described in the following manner. The wax coating on a glass plate is scratched by means of a dividing machine in such a way that etching produces two comb-like "grids" 0·1 mm. apart and 10 mm. in length, which fit into one another. By rubbing colloidal graphite into the "grids" one obtains the well-known electrodes, which are a small distance apart with a long intermediate space. The "grid" plate so prepared is uniformly coated with a thin layer of the selenium-tellurium alloy by means of cathodic sputtering. This process is carried out in an evacuated container in which a piece of the prepared alloy is placed in a

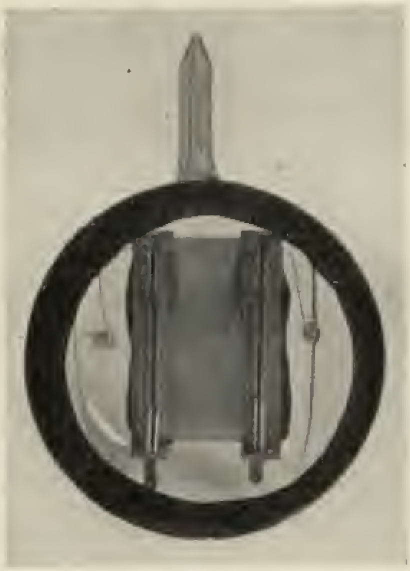

Fig. 1. Selenium-tellurium cell in evacuated glass container.

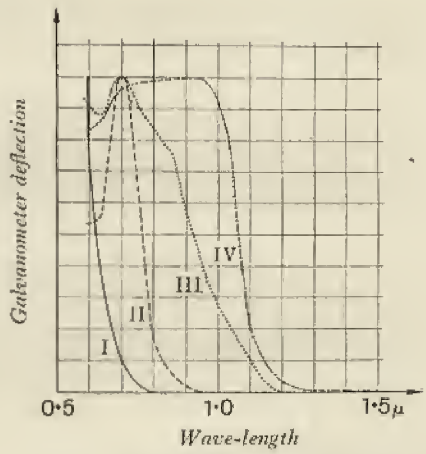

Fig. 2. Wave-length sensitivity curves of various cells.

suitable position relative to the glass plate. Sputtering takes place in argon, the pressure being so regulated that the cathode "dark space" extends half-way to the glass plate. The thickness of the layer is regulated by the time of sputtering, the current being kept at constant strength. The glass plate is then heated in a thermostat for 2 hours at 210°, and this gives the coating the right crystalline consistency and size of grain. Selenium crystals having a different crystalline form differ in their spectral sensitiveness; perhaps, therefore, it may be said that the addition of tellurium assists the formation of the crystalline form of selenium which reacts to light of longer wave-length. The plate, provided with connexions for current, is finally enclosed in an evacuated glass container to protect it from oxidation and atmospheric moisture (Fig. 1).

§4. METHOD OF MANUFACTURE OF THALLIUM SULPHIDE CELLS

We succeeded in preparing highly-sensitive thallium sulphide cells also by a similar process. The thin layer is, however, produced not by means of cathodic sputtering but through thermic vaporisation in a closed container filled with oxygen at a pressure of about 0·8 mm. When the speed of vaporisation is correctly regulated the infra-red sensitive oxygen compound of thallium sulphide is formed. The electrode "grid" (area = 1 sq. cm.) consists in this case of a deposit of gold on a quartz glass plate. Owing to the small distance between the electrodes and their numerous comb-like notches it is possible, even with the extremely thin layer produced by vaporisation, to obtain dark resistances of only $5 . 10^6$ to $10 . 10^6$ ohms, with the same sensitiveness as the Case "Thalofide" cells, whose dark resistances are $100 . 10^6$ to $500 . 10^6$ ohms.

§5. SPECTRAL SENSITIVENESS OF CELLS

Fig. 2 shows the distribution of spectral sensitiveness of thinly-coated selenium cells prepared by cathodic sputtering (I), ordinary selenium cells (II), selenium-tellurium cells (III), and thinly-coated thallium sulphide cells (IV) in the part adjacent to the visible region, up to $1·2\mu$. The curves represent averages obtained from various cells of each kind; the ordinates have been equalised at the maximum points. It will be seen that the effective interval in the infra-red lies between 0·75 and $1·2\mu$. Sensitiveness in the region of longer heat waves can certainly be obtained beyond this by special means, but the absolute amount of sensitiveness falls considerably, so that the practical use of the photo-electric effect would appear nevertheless to be limited to the region between 1·2 and 2μ.

§6. APPLICATIONS OF CELLS

For the purpose mentioned at the outset, cells of the kind described, with a surface of about 1 sq. cm., are placed close in front of the focus of a concave mirror. They are connected by a suitable resistance coupling with a low-frequency amplifier. With a receiver of this kind it has been possible in telegraphy to bridge with ease a distance of 28 km. in the country. The emitter was a 600-watt D.C. arc lamp with a diaphragm containing holes rotating in front of the crater and supplying a frequency of 400 cycles per second. The rays are caused to converge within an angle of $5°$ to $7°$ by a large glass lens. The receiver was fitted with a four-stage amplifier; after the first valve transformer coupling was used. At short distances experiments in telephony were also successful in which at the emitter the modulation of a constant light source was obtained by means of a Kerr cell. The resonance radiation of electrically-excited helium ($\lambda_r = 1·08\mu$) in a gas discharge lamp with a constricted positive light column proved also very sensitive to telephonic influence if the amplified speech current were superposed on the D.C. circuit of the discharge. In all these experiments visible light was eliminated by Wratten infra-red filters (No. 87).

The use of the cells described lies mainly in the sphere of telegraphy and telephony by means of bundles of invisible rays. Haze and slight fog (visual distance for the eye $\gg$ 100 m.) are penetrated noticeably better by wave-lengths above 1μ than by visible light. In very thick fog at 1150 m. above sea level, when the eye could see only about 20 m., the infra-red between 0·75 and $1 \cdot 1\mu$ failed in exactly the same way as light even at quite short distances, less than 1 km., and it seems likely that in this case only the longer infra-red of several μ would be successful. Owing to absorption by the water vapour and carbon dioxide in the air, naturally only distinct regions of the spectrum have then any effect. As bolometers or thermopiles alone seem applicable for the detection of such waves, it would scarcely seem possible to transmit high signal frequencies. One must be content with slow modulations and, for the purpose of determining the direction of the radiator (taking bearings, navigation), must make use of the "Deckfeuer" method to distinguish disturbing radiators. In this method two radiators, one fixed and the other rotating round it, are provided with special slow modulations, one of which is varied in a known manner as the radiator varies its position relative to the other. Thus a special resultant effect corresponds to each direction of the line joining the radiators. The direction is determined by observing the disappearance of the second modulation, which occurs at the instant when the two radiators are in line with the observing station, that is, when the nearer radiator obscures the other.

THE "THALOFIDE" CELL

By THEODORE W. CASE,

Case Research Laboratory, Auburn, New York.

MS. received April 17, 1930. *Read June* 4, 1930.

ABSTRACT. This cell is light-active to infra-red radiation and has its maximum action at a wave-length of about 1 μ. A detailed description of its preparation and characteristics is given. Drawings disclosing its construction and the curve of its spectral sensitivity, together with the transmission curves of infra-red and visible radiation through the atmosphere, are shown. An efficient infra-red filter is described and its transmission curve is given. The circuit employed in infra-red signalling is shown and a brief description of the apparatus and the method of using it is given.

§ 1. PREPARATION OF "THALOFIDE"

In the course of an extended search* for materials that change their electrical resistance on exposure to light, carried on in 1916–17 at the Case Research Laboratory, Inc., Auburn, New York, it was found that oxidised thallium sulphide was very sensitive to the action of the infra-red.

Experience in the preparation of this sulphide—called "Thalofide" because it contains thallium, oxygen, and sulphur—proved that its light activity depended largely on its purity. Therefore only quartz or pyrex glass apparatus was used in its preparation and reactions producing by-products whose removal required prolonged washing were avoided. The method of preparation finally adopted was as follows. The crude ingot metal, containing 95 per cent. of thallium, was melted and granulated by pouring it into water. The granulated metal was dissolved by boiling in dilute sulphuric acid and the solution was evaporated and cooled to separate the thallous sulphate. After purifying the sulphate by three re-crystallisations it was dissolved in water and spongy metallic thallium was obtained from the solution by electrolysis. The current used was about 900 mA.; the electrodes were platinum, and the positive electrode was placed in dilute sulphuric acid on a porous cup partially immersed in the thallium solution. When the electrolysis was nearly completed, the spongy metal was removed from the solution, washed several times with distilled water, and kept under water until used.

To convert the metallic thallium into thallous hydroxide it was placed in a long glass tube which passed through one hole of a cork stopper fitted into the neck of a flask partly filled with boiled, distilled water. A glass tube was inserted in the other hole in the cork for leading oxygen into the flask. After displacing the air in the system by oxygen, the water in the flask was boiled, and as the metal in the tube gradually dissolved the solution flowed down into the flask. Purified hydrogen sulphide was then passed through the hot solution until the thallous sulphide was

* T. W. Case, *Phys. Rev.* (2nd Ser.), **9**, 305–10 (1917).

completely precipitated. The sulphide was filtered by the aid of suction and washed several times with boiled, distilled water. The material was transferred to an electric oven and dried at about 80° C. until its dull black colour began to change to a dark steel grey. This colour change is due to oxidation and it is at this time that most of the light activity of the substance is developed.

The material was then removed from the oven for test and the process of drying for short periods and retesting was repeated until the required sensitivity was attained. The test for sensitivity was made in the following manner. The powdered thalofide material was dusted on a hot, three-quarter inch quartz disc and the excess of the melted substance was removed by a single stroke of a steel straight edge across the surface. Conducting lines of graphite were then drawn on the coating and the ends of alternate lines were connected. The test disc was mounted on a support and placed at the end of a box about 8 ft. long in which was a movable photometer light having a tungsten filament. The graphite lines on the disc were connected in series with a galvanometer and a 45-volt battery and the dark resistance of the coating was read. The photometer light was then turned on and moved until the galvanometer deflection showed a 50 per cent. decrease in the resistance of the coating. When 1 foot-candle of illumination from the photometer light produced this decrease in the resistance of the coating the drying process was discontinued and the thalofide material was transferred to glass tubes, evacuated, and sealed off to prevent further oxidation.

§ 2. MANUFACTURE OF CELL

In making the "Thalofide" cell, the disc was coated as it was for the sensitivity test but the conducting lines, placed on the coated surface, were of lead and were sprayed on with a Schoop metal-coating pistol to form a better contact. The disc was then mounted on a stem, sealed into a tube and evacuated. Helium at about 500 mm. pressure was then let into the tube, which was sealed off and removed from the vacuum pump. This treatment not only preserved the life of the element by preventing further oxidation but it also increased the sensitivity of the thalofide coating from three to five times.

Helium was used in the cells because it was found that in work on picture transmission and in talking-picture sound reproduction less lag was observed in the action of helium gas-filled cells than in high vacuum cells. This difference is presumed to be due to the cooling action of the helium which has a very high thermal conductivity.

The upper drawing of Fig. 1 represents the coated surface of the disc after the lead has been sprayed on. The heavy black line shows the thalofide coating. The lower drawing of Fig. 1 represents a longitudinal section of the finished cell.

§ 3. CHARACTERISTICS OF CELL

The average sensitivity of the cells is such that the dark resistance is lowered by 50 per cent. in less than 0·25 foot-candle when the source is a tungsten filament. Cells have, however, been made which lowered their dark resistance by 50 per cent. in 0·06 foot-candle.

During the evacuation process and thereafter the cells cannot be exposed to more than 0·5 foot-candle of light without serious injury, such exposure causing them to lose high resistance and sensitivity and to become unsteady in their action.

Fig. 2 shows the spectral sensitivity curve of the "Thalofide" cell as determined by Dr W. W. Coblentz of the Bureau of Standards at Washington, D.C. This curve shows that a very large part of the action of the cell is caused by the infra-red just beyond the visible red of the spectrum.

Other characteristics of the "Thalofide" cells which may be noted are their almost instantaneous return to their dark resistance after exposure to low light intensities and their high resistance as compared with the selenium cell, the resistance of the cells in the dark ranging from 5 to 500 megohms.

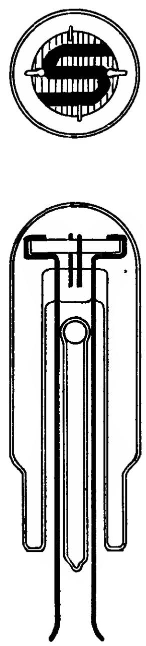

Fig. 1. Construction of "Thalofide" cell.

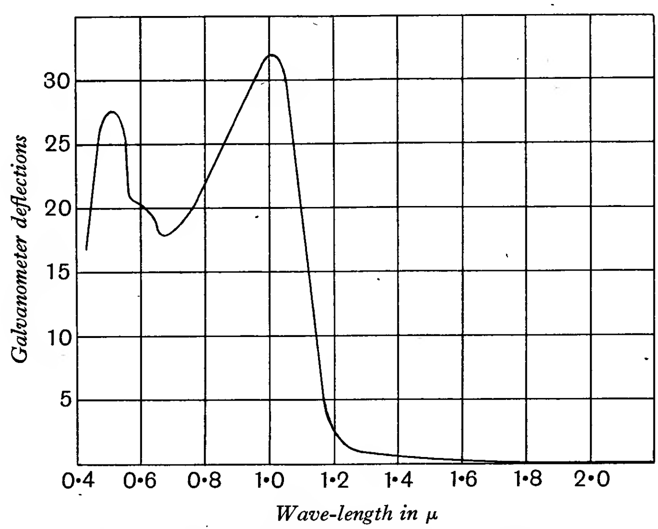

Fig. 2. Spectral sensitivity curve of "Thalofide" cell.

The curves in Fig. 3 show that the infra-red rays are transmitted through the atmosphere with less absorption than the visible rays on a reasonably clear night. The transmission of the infra-red was detected by a "Thalofide" cell and a galvanometer, and the readings in the visible spectrum were taken with a Sharp-Millar photometer.

§ 4. APPLICATION TO SECRET SIGNALLING

As the "Thalofide" cell was developed with the idea of using it for secret signalling it was necessary to devise an efficient light filter that would transmit the infra-red but not the visible rays. By testing different combinations of Wratten filters it was discovered that, when Nos. 91, 45, and 53 were superposed, no visible

light was transmitted but about 80 per cent. of the infra-red came through. A combination of the dyes used in these three filters was made in a gelatine film which was coated on optical plate glass. The film was protected by a suitable cover glass and the edges of the filter unit were sealed to prevent moisture from attacking the

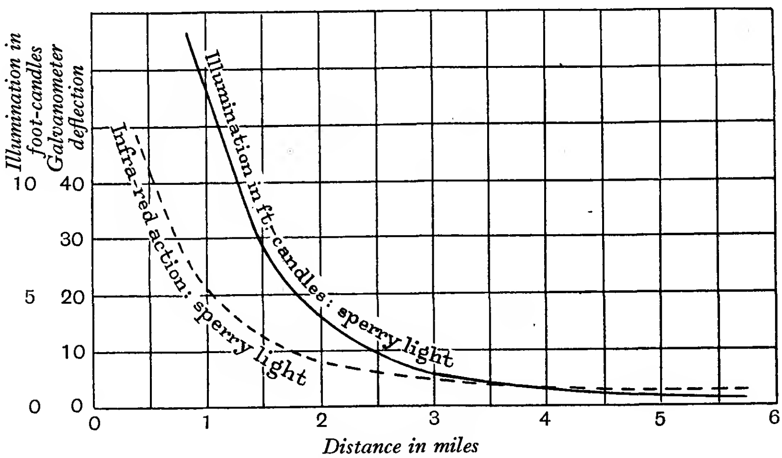

Fig. 3. Transmission of infra-red rays through the atmosphere.

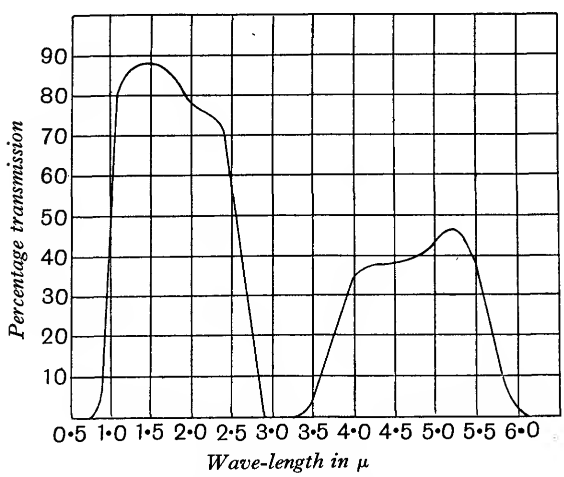

Fig. 4. Transmission curve of infra-red filter.

gelatine. Fig. 4 shows the transmission curve of the infra-red filter as plotted by Dr W. W. Coblentz.

In an efficient infra-red signalling system the signals detected by the "Thalofide" cell should be made audible. To accomplish this the circuit shown in Fig. 5 was devised. The audion bulb used was of the Western Electric V type and contained argon at the proper pressure to allow the bulb to oscillate freely at a minimum

voltage. The cell potential totalled 200 volts and was variable to take care of the differing dark resistance of the cells.

The action of the "Thalofide" cell in this circuit may be compared with that of a valve through which a positive potential builds up on the plate until a discharge occurs through the gas of the bulb to the negative. The time rate of the building up of consecutive charges and discharges is varied by increasing or decreasing the resistance of the cell. The succession of charges and discharges, of course, causes an audio-frequency note to be heard continually in the phones. When the resistance of the "Thalofide" cell is lowered by an incoming signal the time rate of charge and

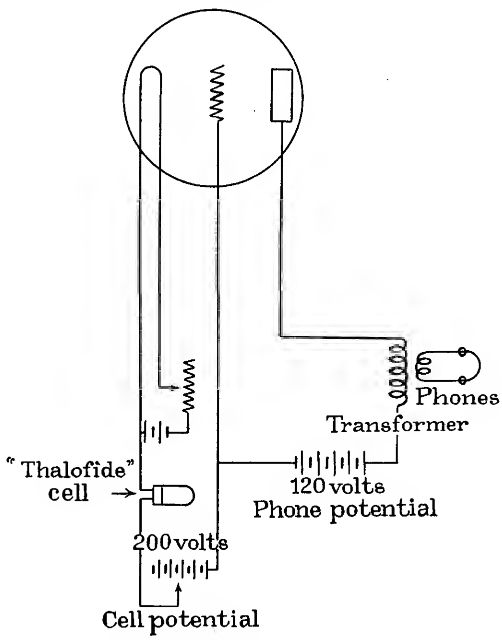

Fig. 5. Circuit for infra-red signalling.

discharge is varied and a change of pitch in the audio-frequency note is heard in the phones.

In actual signal work the "Thalofide" cell is placed at the focus of a parabolic mirror which acts as a collector of the infra-red beam. Any suitable searchlight which is properly screened with an infra-red filter, and provided with a means for interrupting the beam for dot and dash signals, may be used for a projector.

Some of the first official tests of this apparatus were made before representatives of the Army and Navy in October 1917, between Fort Hancock and the Woolworth Building, New York City, a distance of about 18 miles. Messages were successfully transmitted and the signals were so loud that they could be heard at some distance from the phones. These results were obtained in spite of the usual smoky atmospheric conditions between these points. The sending apparatus consisted of a 60-in. Sperry searchlight situated at Fort Hancock and screened by an infra-red filter. The receiving apparatus consisted of a 24-in. parabolic mirror with the

"Thalofide" cell at its focus. The "Thalofide" cell was connected to the oscillation circuit described above.

This system was also adapted for infra-red telephony by the use of a special manometric flame as the source of the transmitting beam. At the receiving end the "Thalofide" cell was connected to a straight hook-up for simple and direct amplification.

For further descriptions and details of the uses of the "Thalofide" cell in secret signalling see an article by the author on "Infra Red Telegraphy and Telephony," published in the *Journal of the Optical Society of America*, **6**, No. 4, 398–406 (1922).

GENERAL DISCUSSION*

Dr N. R. Campbell. Prof. Allen in his introductory lecture described the invention of the "black-body" cell as a great advance. It ought to have been, but actually it was not; the adoption of the black-body principle does not actually increase the effective sensitivity by as much as 50 per cent. The reason is probably that the surface absorbs very strongly that part of the radiation which excites the photo-electric emission.

Mr H. R. Ruff. With reference to the paper by Dr Campbell on "The standardisation of photo-electric cells," the British Thomson-Houston Co. agrees that some such standardisation is very necessary. The majority of our cells are used for sound reproduction, and, since we have some hundreds of sound-reproducing equipments operating or in the course of manufacture, we are directly interested. We feel, however, that the matter is really one for consideration by a small committee of those concerned.

In Dr Campbell's paper is included a diagram suggesting limiting dimensions for cells manufactured to operate in sound-reproducing equipments. While the proposed height of the centre of the spot of light from the base of the cell is roughly that employed in the B.T.-H. sound reproducer, cells with the overall dimensions given would be too large to fit into these equipments, and we could not adopt these figures.

We have, of course, established a specification under which cells are manufactured as suitable for our own sound reproducer. Such a specification is of necessity made as brief as possible. The dimensions of the cells are specified, and the sensitivity and uniformity of the production controlled by limits on the primary emission and gas amplification of the cells, when checked with a light source equivalent to that used in the reproducer.

Owing to the diversity of cells at present manufactured, a somewhat extensive series of tests is necessary to adjudge the merits of cells of different types and makes. Our practice is as follows:

1. With a low anode voltage (of the order of 12 volts) the uniformity of emission from different parts of the cathode surface is measured.

2. Provided the cathode is fairly uniform, a wave-length sensitivity curve showing the response of the cell to equal amounts of energy of different wavelengths is then taken with the low anode voltage applied. This curve at once gives an idea of the primary emission of the cell when used with a light source of known energy distribution.

3. With gas-filled cells readings are taken showing the sensitivity of the cell, in microamperes per lumen, plotted against anode voltage. This curve is taken with a tungsten gas-filled lamp of known temperature as the light source. A curve showing the variation of glow voltage with light is next taken and, regarding these two curves simultaneously, some idea of the output obtainable from the cell with

* [The order of the remarks in this report follows that in which the corresponding papers appear rather than that of the actual discussion.—Ed.]

a given intensity of illumination from the lamp can be gained. The curve showing the variation of glow voltage with light flux is necessary since different types of cells possess different characteristics in this respect. For example, a thick-film potassium cell may possess a characteristic differing from that of a thin-film caesium cell.

4. Finally, a measurement is made as to the variation of the photo-electric current with light for constant anode voltage. This is taken with the low anode voltage of 12, giving approximately the primary emission of the cell cathode surface. Then a second curve is taken with an anode voltage giving a specified amplification of the primary emission by the gas-filling. If the glow voltage of the cell is considerably in excess of the latter voltage a third curve is taken using a higher gas amplification figure.

5. The insulation of the cell is measured at its working voltage.

The curves obtained from these tests, viewed collectively, give a good idea of the suitability of a cell for any particular light source, and the sensitivity obtainable when used in conjunction with it. There are other features worthy of note, such as the suitability of the mechanical design of the cell for a particular use, while, when considering the gas amplification available, the stability and life of the cell and the frequency of intermittence of the light falling on the cell are points of importance.

Dr N. R. Campbell. There are three points in Mr Ruff's remarks on which I should like to ask questions.

(1) He says that the variation of the glow voltage with the illumination is less in cells with caesium cathodes than in those with potassium cathodes. My experience is that this variation depends almost entirely on the geometrical form of the cell and little on the nature of the cathode; it is least when the electrodes are approximately parallel planes and greatest when the anode is very small compared with the cathode. Were the cells that he compared of similar geometrical form?

(2) How great are the variations in emission that he finds over the surface of a single cathode? Our experience is that in satisfactory thin-film caesium cells the variation does not exceed 25 per cent. on either side of the mean, and is often very much less; if it is greater, the cell is usually defective in some other respect. Is that also his experience?

(3) Can he give us any figures concerning the life of cells? We have made some life tests, subjecting cells to a current of about 1 microamp. at the highest anode voltage possible with such a current. We find that, apart from changes in the first hour, the emission falls off somewhat during the first 200 or 300 hours, decreasing perhaps 30 per cent. After that time the results are irregular; some cells show no further change, others may be subject to large and irregular variation.

Mr H. R. Ruff. (1) The cells we compared were not of exactly the same geometrical shape although they were not markedly dissimilar. Dr Koller* has, however, compared potassium and thin-film caesium cells of the same construction and states that the emitting surface is a factor in determining the glow point.

(2) In general the emission of the cathode surface of the thin-film caesium cell is fairly uniform, varying within the limits mentioned by Dr Campbell. We have not experienced difficulty with cells giving wider variation.

* Koller, *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **19**, 138 (1929).

(3) Our experience is that the output of the cells is liable to change during the first few hours of life, in the majority of cases increasing, and that subsequently the output falls gradually during life. The behaviour of the cells is fairly uniform, only an occasional cell showing irregular variation.

Dr N. R. Campbell. With regard to the question of the variations between different cells of the same type, our experience is that, if a comparatively low standard of emission is set, there is never any difficulty in producing large batches of cells that do not differ from this standard by more than 10 per cent. But occasionally, and especially in the production of thin-film cathodes, cells are obtained that give an emission very much greater than the standard. These cells get into the hands of a customer, who is then inclined to demand that all cells should be up to this standard. That is why we have to set very wide tolerances to the emission of our cells. Of course we desire to make all cells up to the higher standard, but at present we are not able to achieve that, and it seems wasteful to reject cells on the ground that they are too good.

Mr L. H. McDermott. The question of variability after similar processes of production has been raised, and it might be of interest to know that at the National Physical Laboratory we examined two cells for spectral sensitivity and found that, although made under identical conditions, they had maxima one at $\lambda 4800$ and the other at $\lambda 6800$.

Mr H. de Laszlo (communicated). It is customary among photo-electric cell manufacturers to compare cells on the basis of plots showing the relation between photo-electric current and light intensity in lumens. Now light sources, having entirely different energy distributions in the visible spectrum, may appear to the eye to be of the same intensity in lumens, but would produce entirely different currents in a photo-electric cell. Such plots, therefore, do not have a great deal of meaning, and do not furnish a proper basis for comparison of photo-electric cells.

I would, therefore, like to suggest that all vacuum cells should, at least, have their response curves given in terms of coulombs (response) per erg (incident energy) at each wave-length. Expressing results in such absolute units enables one to compare the sensitivity of various surfaces at given wave-lengths, and is an indication as to the adaptability of such a surface for any special purpose. The approach to the maximum possible response, or percentage efficiency, is not at all apparent however, when results are expressed in coulombs per erg. If the response is given in electrons (liberated) per quantum (incident energy) the approach to the maximum possible response is immediately seen.

The only way in which the photo-electric efficiency can be completely specified is by means of a curve which shows for any wave-length the corresponding efficiency. This curve will be similar to the wave-length distribution curve in shape, the only difference being that the efficiency curve is for an "equal quanta" spectrum instead of for an equal energy spectrum. Obviously, if one point on a wave-length distribution curve can be expressed in absolute units (coulombs per erg or electrons per quantum), the photo-electric efficiency at any wave-length can be found at once.

As examples of how inefficient photo-electric cells still are, I give in the accompanying table a set of measurements for two modern vacuum cells with quartz

windows. A great variety of metallic surfaces have been measured in this way and the results will be published in due course.

Wave-length Å.U.	Sodium on silver Coul. Erg × 10^{-12}	Sodium on silver Electrons Quanta	Magnesium Coul. Erg × 10^{-12}	Magnesium Electrons Quanta
5461	2·5	·000057	—	—
4350	56·5	·00161	21·6	·00061
4040	137	·00419	—	—
3656	260	·00855	57·7	·00195
3341	432	·0160	—	—
3130	621	·0245	252	·00987
2967	430	·0179	427	·0178
2890	—	—	540	·0231
2804	338	·0149	738	·0326
2699	305	·0140	—	—
2652	295	·0138	1200	·0562
2536	274	·0133	1330	·0650
2483	260	·0130	1260	·0628
2399	252	·0130	792	·0408

Mr L. J. DAVIES. Is it possible to construct the Selényi type of gas-filled cells by putting in the gas before obtaining the oxygen from the glass?

Dr P. SELÉNYI (communicated). Since we have not experimented much with gas-filled cells, I am unable to give a definite answer. When the cell is filled with argon at a pressure of 0·1 to 0·5 mm., the oxidation of the sodium mirror does not appear to take effect so readily, and it is difficult to obtain the coloration which is so characteristic of the sub-oxidation. On the other hand, we frequently found that cells, in which the sodium mirror has remained silver white in spite of the oxygen filling, are sensitive to red.

Dr J. H. J. POOLE. What is the method of introducing oxygen electrolytically if the cell is originally highly evacuated?

Dr P. SELÉNYI (communicated). On account of patent rights I have purposely avoided the method of introducing oxygen electrolytically and would therefore prefer to leave this question unanswered.

Prof. F. A. LINDEMANN. I am interested to see from the paper by Dr Campbell and Mr Stoodley that, whereas his curves show that the inertia of the potassium cells is negligible, at any rate up to one five-thousandth of a second, there is an appreciable falling off in the response of the caesium cells even at frequencies of 500 per second. Such slow rates of response seem to indicate that in these cells we are dealing with chemical processes rather than purely electronic reactions. Probably this is to be expected in cells whose sensitivity maximum is towards the red end of the spectrum since presumably this shift is caused by some chemical interaction between the metal and the other substances employed.

Dr N. R. CAMPBELL. I quite agree that no pure electronic theory will account for time-lags as large as are actually found. But the difficulty of any chemical theory seems to be to account for the continuance of the current after the light is turned off, and the complete independence of the *mean* current on the frequency; on these grounds all theories based on a change of the emission of the cathode are inadequate. At one time we suspected that some kind of phosphorescence might

be responsible, for we have found that the passage of large currents through the gas produces a faint glow, even at voltages well below the glow potential; but we have no real evidence in favour of that theory.

Mr G. T. Winch. I am particularly interested in the paper by Dr Dobson and Dr Perfect, as I had occasion about three years ago to build an amplifier of the type used by Dr Clayton Sharp for photometric purposes and similar to that described by the authors. This was in connexion with the development of photo-electric photometers for the commercial measurement of incandescent electric lamps. With this apparatus the best repetition accuracy I obtained was about 1 to $1\frac{1}{2}$ per cent. in lumens. The limitation of accuracy was due to the galvanometer fluctuations referred to by Dr Dobson. Partly for this reason, and partly because a type of photo-electric cell particularly suitable for photometric work became available, I found it more convenient subsequently to utilise the linear relation between photo-electric current and illumination on the cell in conjunction with a "valve bridge" amplifier. It is very interesting to note that the authors' apparatus is capable of detecting a change of 10^{-15} amp. as this should make it possible to use this method for high precision photometry.

Mr H. A. Thomas. With reference to Mr Yates-Fish's paper, I would like some more information as to how equation (4) is derived. It appears from the equation that R_a and R_e have been taken in parallel and then the net resistance taken in series with C and G. The solution of the circuit considered is far more complex.

I do not think that the amplifier used had anything like the voltage amplification required to give the "Schrot" effect. The instabilities mentioned are far more likely to be due to commutator and other causes. The amplification required to give appreciable "Schrot" effect is of the order of 10^6, whereas for the three stages considered the amplification is theoretically only 15,000 and probably actually about 6000.

Mr N. L. Yates-Fish. In reply to Mr Thomas, the method given in paragraph 1 of my paper is admittedly an approximate one; its value lies in the rapidity with which it enables the general behaviour of the amplifier to be predicted. With regard to equation (4), it is not difficult to prove that the valve with its coupling resistance is equivalent from the point of view of the galvanometer circuit to a generator whose internal resistance is given by R_a and R_e in parallel and whose E.M.F. is m times the grid voltage.

Dr G. M. B. Dobson. Mr Thomas has pointed out that the input impedance of the amplifier which we use depends on the characteristics of the galvanometer, etc. in the output circuit. When the commutator is running the output circuit will be either short-circuited or broken at the moment of reversal. This must change greatly the characteristics of the output circuit and therefore, according to Mr Thomas, also the input impedance of the amplifier. Can Mr Thomas tell us whether this might result in the fluctuations which we observe when the commutator is running? Also what is likely to be the effect of the continuously variable commutator, which we have suggested, in this respect?

Mr H. A. Thomas. With reference to the remarks of Dr Dobson, I think it

extremely likely that the variable impedance in the output circuit produced by the rotating commutator may account for some of the fluctuations noticed. Although the continuously variable commutator suggested will not eliminate this effect, it will make it periodic and will eliminate transient effects to a very considerable degree. I shall be very interested to see the outcome of experiments along these lines.

Prof. CHARLES A. CULVER. As one who is interested in the physics of the photo-electric cell, I regret that we were unable to hear Drs Geffcken and Richter present their paper in person, because I feel that the introduction of a third electrode (control) may serve to give us some valuable information regarding the fundamental processes involved. Has anyone present had any experience in the use of such a third electrode?

Dr N. R. CAMPBELL. Many proposals have been made to use photo-electric cells with third electrodes, or grids, for various purposes, but they all encounter the difficulty that it is almost impossible to prevent the third electrode becoming coated with light-sensitive material and therefore acting as cathode as well as grid.

Drs H. GEFFCKEN and H. RICHTER (communicated). The auxiliary electrode 6 in Fig. 5 of our paper acts not as a grid, but as a second anode, in which the emission of electrons is of no significance and, on account of the fixed (positive) potential, practically does not come into consideration.

Dr N. R. CAMPBELL. I cannot understand why Dr Harrison is so concerned about "dark current." In a cell provided with guard-rings there is, or ought to be, no dark current comparable with the photo-electric currents of the order which Dr Harrison must be using. Again, nobody has produced any evidence whatever that, in a well-constructed vacuum cell (this proviso is important), there is any departure from strict proportionality between light and current. On the other hand, there may be some change of the emission with time, especially if the cathode is well insulated thermally by being supported in a vacuum; for then the incident radiation may heat the cathode appreciably and cause alterations in it. For this reason it is important not to throw more light on the cathode than is necessary to obtain the requisite sensitivity. In the routine photometry conducted at Wembley it is found that the emission of a cell does not change by more than $1\frac{1}{2}$ per cent. during a day's work.

Prof. F. A. LINDEMANN. I am much interested to hear Dr Campbell express the opinion that the change in sensitivity might be due to a change in temperature of the cathode. This would seem evidence in favour of the view I suggested that the sensitive cells owe their sensitivity to some chemical reaction. It would be quite reasonable to expect this to depend upon the temperature and this would be in harmony with the explanation put forward by Dr Campbell.

Dr T. H. HARRISON. I am pleased to hear that the more recent thin-film photo-electric cells are not subject to such large variation of sensitivity, when exposed to illumination, as those found about a year ago by me. I do not think that, with the curves which I have shown, the illumination was sufficient to produce observed change of sensitivity by virtue of the heat received by the cathode of the cell. The illumination was considerably smaller than that used in most applications of photo-electric cells. It is, however, only two years since the introduction of thin-film

cells, and it is only reasonable to suppose that more recent specimens than those which I tested have a more constant sensitivity. I agree with Dr Campbell that a perfectly made vacuum photo-electric cell would obey the proportionality law. It would also serve as a standard of light sensitivity. Progress towards this perfection has been made in the Elster and Geitel blue-sensitive type, and improvements in gas-filled cells have been concurrent with those in vacuum cells, the faults of the former not exceeding by much, if any, those of the latter. Similar progress will undoubtedly be made with the thin-film cells, but I doubt whether they will become less subject to the faults of non-proportionality and lack of constancy in sensitivity than the thick-film type.

Dr J. W. T. Walsh. There is just one question I should like to ask Dr Harrison or anyone present who may have had experience in the matter. All who are interested in industrial photometry know that there is a great demand at the present time for polar curve determinations on lighting fittings and the only thing which limits this demand is the amount of work involved and the consequent cost. If anything can be done to reduce the work it would be of very great benefit to the industry. It occurred to me on reading the papers by Dr Sharp and Dr Harrison that it might be possible to achieve this by substituting a photo-electric cell for the eye on the photometer bench and passing the current through a galvanometer, the spot of light from which falls on a piece of photographic paper attached to the rotating mirror of the polar curve apparatus. In this way an automatic record of the polar curves might be obtained. I do not think the idea is new but I am not aware that it has been adopted to any great extent in practice and I should like to know whether there are any difficulties which would render it impracticable.

Mr G. T. Winch. This is a line of development on which I have been working, and an apparatus for tracing polar distribution curves is in course of construction which I hope will be capable of drawing a complete curve on the standard sizes of paper used for this purpose.

Dr T. H. Harrison. The measurement of polar curves of electric lamp fittings by means of photo-electric cells, with a degree of precision exceeding that of the visual method and in a manner involving an expenditure of far less work and time, is certainly a practical proposition. Some very ingenious photo-electric photometers designed for the purpose of measuring polar curves have been made and described by Horioka and Sato*. In these, commercial accuracy is all that has been sought for. In one of these systems, the image of a galvanometer scale, as observed through a rotating mirror, is caused to rotate about a zero point of the scale. In this manner the deflection of the galvanometer spot lies in the direction of a radial arm, with the result that the spot can be made to trace out a polar curve of the fitting which is being tested. Persistence of vision allows the path to be seen as a continuous bright curve. In my opinion the time is not far off when the visual plotting of polar curves of lamps and fittings will be entirely superseded by the photo-electric method.

Prof. F. L. Hopwood. I would like to ask Dr Poole whether his neon lamp

* M. Horioka, *Japanese Patent* No. 71670 (1926); M. Horioka and T. Sato, *Researches of the Electrotechnical Lab. Tokio*. No. 213 (1927); M. Horioka, *ibid*. No. 268 (1929).

photometer is, or could be made, sufficiently sensitive to detect by its γ-ray effect the presence at a distance of a few feet of a milligramme of radium. A portable device for this purpose which could replace an electroscope would facilitate the search for missing radium needles.

Dr J. H. J. POOLE. The neon lamp photometer method is at present not sensitive enough. There is a direct effect of γ-ray radiation, but this effect seems rather erratic and only produced by fairly strong γ-ray illumination. It might however be possible, by reducing the self-capacity of the tube and greatly improving the insulation, to detect the ionisation current produced by small sources, but personally I feel rather pessimistic in this direction.

Mr WILLIAM GAMBLE. I think Professor Koch has done well to stress the importance of the photo-electric cell as a light-sensitive detector in the measurement of photographic densities, as no doubt it will find an increasing application for that purpose. An instrument has already been constructed for measuring the opacities of photographic negatives by means of the photo-electric cell. The method consists in photographing a standard grey patch along with the photograph or other object which is being copied and the image of this patch on the negative is measured by the instrument to determine whether it corresponds to the density adopted as a standard. By this means it has been found possible to balance correctly the densities of a set of three-colour negatives. If the platemakers were to adopt some such system of testing it might be possible to obtain more uniform plate speeds in different batches than are obtained by present methods.

Dr F. C. TOY. I would like to clear the characters of the British manufacturers of photographic materials by saying that they have been using photo-electric photometers for some years now for measuring photographic densities.

Mr T. SMITH. The advantages of the photo-electric cell in photometry and spectrophotometry lie, as Dr Gibson has pointed out, in the saving of time and the close reproducibility of the results. Ultimately one hopes that the latter property can be utilised in such a way as to yield greater accuracy than is easily attainable with visual measurements. The importance of such an advance in physical measurements is obvious. One of the developments on which Dr Gibson has something to say is the application of photo-electric cells to colorimetry, and in this field I feel that even more caution than Dr Gibson displays is needful. There are clearly numerous limited fields of great industrial importance where the difficulties to be faced are comparatively trivial, but the problem of photo-electric colorimetry over the whole range of visual sensations is decidedly not one of these. It is notorious that colorimetry via visual spectrophotometry is often not colorimetry at all. There remains the possibility that photo-electric spectrophotometry may at some future time be more successful. I fear that the reference by Dr Gibson to the well-known visibility tables for which he is partly responsible may be somewhat misleading since it occurs in a discussion on colorimetry via spectrophotometry. These tables are sufficiently accurate and have been valuable for certain technical purposes but they definitely fail to reach the accuracy required for colorimetry. It must be emphasised that for colorimetry there is no international agreement on the values that should be used. Thus at the present time there is an essential link missing in the chain that must be completed before general photo-electric colorimetry is possible.

If we assume that ultimately we shall have adequate knowledge of the relation between sensation and stimulus in human vision, a question of importance may arise. We may be able, on the basis of photo-electric measurements, to differentiate between the physical properties of materials to a degree of accuracy too fine to involve a corresponding difference of sensation. The question will then arise whether we ought to say that the colours are alike or that they differ. Perhaps the physicist will incline to the latter alternative, but I suggest that such a choice is mistaken. Workers in the field of colour sensations are already seriously handicapped by the way in which the physicist has appropriated sensational terms instead of constructing more suitable words for the associated physical concepts, and I suggest that there would be a definite gain if a stricter attitude were adopted. It will perhaps come as a surprise to most physicists that even such a well-recognised term as "monochromatic" causes sufficient difficulty to have led some of us to substitute "monorhythmic" for it when the concept involved is physical.

Prof. F. A. Lindemann. Mr Smith has called attention to a certain lack of logic in counting two substances as having different colours because the photo-electric cell shows the difference whilst the eye shows none. From the metaphysical standpoint he may be right, but I would suggest that the physicist understands by the word "colour," not the subjective impression caused by the light reflected from a given substance, but the curve representing its reflection coefficient as a function of the wave-length. From the physicist's point of view, therefore, two substances will have identical colour only if their reflection coefficients are the same for all wave-lengths. Such substances will appear identical to the eye no matter what the source of illumination. Substances which do not have the same reflection coefficients at all wave-lengths may well appear indistinguishable to the eye in certain illuminations, but in principle it would always be possible to find some form of illumination in which the two would appear different to the eye. It would thus appear justifiable to use photo-electric cells for colour-matching, even though they exceed the sensitiveness of the eye, since they will ensure that the two colours are indistinguishable for widely different sources of illumination.

Dr K. S. Gibson (communicated). I quite agree with Mr Smith regarding the need for caution in applying the photo-electric cell to colorimetric problems. Such use of the photo-electric cell is, of course, not the primary subject of the paper. It enters into consideration because the spectrophotometric method is the most fundamental way of analysing colour stimuli and of deriving colorimetric specifications, as I attempted very briefly to indicate in the paper, and because the photo-electric cell furnishes one (out of several) of the methods of obtaining spectrophotometric results. Discussion of all other colorimetric uses of the photo-electric cell was purposely avoided.

I do not understand the objection to the use of the internationally adopted visibility values. The use of such data enables computation to be made of one of the three quantities which are of most importance in colorimetric specification, viz., the light transmission (or relative brightness) of a given material for a specified source. (The other colorimetric quantities, dominant wave-length and colorimetric purity or their equivalents, cannot be computed from visibility data but may be computed from "excitation" data). In view of the well-known differences among the visi-

bility functions of various normal observers (see *Bur. Stand. Scient. Papers*, No. 303, Fig. 13, and No. 475, Table 2), it is not apparent how the international values "definitely fail to reach the accuracy required for colorimetry." They are as suitable as any other values for the computation of minute differences in relative brightness. Furthermore, Crittenden and Taylor ("An interlaboratory comparison of colored photometric filters," *Trans. I.E.S.* **24**, 153–207 (1929)) have shown that values of light transmission computed from spectrophotometric data via the visibility function give very satisfactory agreement with directly measured values. Certainly it would take extensive investigation to demonstrate that the internationally adopted visibility data do *not* accurately represent (except possibly in the end regions of the visible spectrum) the average for a large number of normal observers under standard photometric conditions. I do not see why the present visibility values are not as suitable for use in colorimetry as in photometry or why revision of the values would be of any assistance in making "general photo-electric colorimetry" possible.

Mr Smith's suggestion that the same terminology should not be used to describe both the sensation and the stimulus is well made. It is wholly in line with the definitions and recommendations made by the Colorimetry Committee of the Optical Society of America in 1922 (see *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **6**, 531–42) and by the colorimetry section of the Bureau of Standards for many years (see, for example, Priest, "The colorimetry and photometry of daylight and incandescent illuminants by the method of rotatory dispersion," *Journ. Opt. Soc. Amer. and Rev. Scient. Instr.* **7**, 1176–9 (1923); "Apparatus for the determination of color in terms of dominant wave-length, purity and brightness," *ibid.* **8**, 174–6 (1924)). It is to be hoped that the physical and the psychological aspects of colorimetry will be more clearly differentiated in the future than they have often been in the past. Such distinctions will greatly clarify discussions in this subject.

Dr N. R. Campbell. Dr Perfect has described many methods of using photoelectric cells for spectrophotometry. What seems to be needed now is that their relative advantages and disadvantages should be settled. It would be very instructive if those present who have used different methods would criticise frankly each other's arrangements.

Dr W. R. G. Atkins. With regard to Mr Griffith's use of the cadmium cell for the photometry of the anti-rachitic ultra-violet portion of the spectrum, I may say that I have used the Burt sodium cell for this purpose. Even the glass cell is sensitive to much of the radiation of therapeutic value, as may be shown by interposing a sheet of Pyrex glass—which is known to cut out the anti-rachitic radiation completely. The current is reduced by 25 per cent., which comprises reflection loss and the anti-rachitic. One can thus measure the latter by difference, using a portable microammeter, the source being a mercury vapour arc. Colour filter cells recently devised in the Eastman Laboratories at Rochester give a good correlation between what is measured by the cadmium cell and the erythema curve.

In order to measure ultra-violet from the sun and sky the cell must be designed in a form differing from that of the cadmium cell usually sold for measuring the therapeutic radiation of lamps which can be placed vertically over the cell. A plane sensitive surface beneath a plane glass surface would probably be an improvement

on the usual form. One would prefer to use a diffusing surface placed over the cell, but even thin milky silica sheet cuts down ultra-violet radiation very greatly. It might be possible to obtain diffuse ultra-violet by using a small sphere coated with a white lead pigment internally, and having two windows at right angles. Of these one, placed horizontally, would admit the light from the sky and the other, placed vertically, would be occupied by the photo-electric cell.

As regards Prof. Shelford's paper, I wish to acknowledge that it was his work with Prof. Gail, in the Puget Sound in 1922, which started Dr Poole and myself on our photo-electric photometry in the English Channel. From the present paper I see that Prof. Shelford now checks his gas-filled cell against a vacuum cell, a practice which we regard as most necessary.

Mr Ernest Rostás. I would like to ask Prof. Thirring how he compares the sensitivity of an alkali cell with that of a selenium cell? The one gives a certain current for a given flux, whereas in the other the resistance is changing by a certain percentage for a given light flux.

Prof. H. Thirring. An equal amount of intermittent light has to be thrown on both cells, which are connected to the same amplifier, the coupling capacities and resistances being chosen separately for each cell according to its impedance. The efficiency of the cell may then be measured by the output energy.

I would like to know what is the sensitivity of an average good gas-filled alkali cell, expressed in microamps. per lumen.

Mr L. J. Davies. The average sensitivity is approximately 40 microamps. per lumen.

Prof. H. Thirring. It does not seem to be generally recognised how much greater is the sensitivity of the selenium cell than that of the alkali cell. An example may serve to illustrate this. The area of the light sensitive surface of our selenium cells (type A_{10}) is 10 square millimetres. Hence with an illumination of 100 metre-candles the light flux striking the selenium surface is about $8 \cdot 10^{-5}$ Hefner lumen. With the average cells of that type the additional current at a voltage of 12 volts caused by this illumination is about 6 microamps. The sensitivity of these cells is, therefore, approximately 75,000 microamps. per lumen against 40 microamps. per lumen in the case of the alkali cells. With higher voltages and with specially prepared selenium cells the sensitivity may be even increased to 1,000,000 microamps. per lumen. Certainly these data refer only to continuous illumination, that is to say, to the bottom part of the response-frequency curve. Still, as has been pointed out in my paper, even at frequencies above 10,000 cycles the sensitivity of the selenium is greater than that of the alkali cells. This can be proved by simply replacing the photo-electric cell of any sound film reproducing set by a small area selenium cell, provided that all the available light is thrown on to the light-sensitive surface by means of a suitable optical system.

Dr N. R. Campbell. Prof. Thirring has said that the superior sensitivity of selenium cells enables fewer stages of amplification to be used in talking film apparatus. Will he tell us how many stages he requires to produce from a talking film 40 watts of audio-frequency current?

Prof. H. Thirring. The reproducing sets in which alkali photo-electric cells

are employed, as, for instance, Western Electric or R.C.A. Photophone or Klangfilm sets, are usually equipped with a three-stage input amplifier connected to one or two stages of power amplification. By using selenium cells one stage of the input amplifier may be saved.

Dr N. R. Campbell. Well, we use also three stages to produce 40 watts from a photo-electric cell.

Prof. A. O. Rankine. I intervene to try to resolve the apparent contradiction between the statements of Prof. Thirring and Dr Campbell. There is in my view no need to differentiate between selenium cells and alkali photo-electric cells by attributing the effect in the former to change of resistance and in the latter to the production of a current. In both cases an applied voltage is necessary to produce the change of current arising from illumination. If it is justifiable to speak of the resistances of a conducting system which does not obey Ohm's law, then the term may be applied equally to selenium cells and alkali cells in the sense of meaning the ratio of applied voltage to current, and for both this ratio is a function of the voltage as well as the illumination.

This, therefore, is not the explanation of the difference between Prof. Thirring and Dr Campbell. Both in fact are right if we distinguish between "amplification" and "stages of amplification." There is, I think, no doubt that the changes of current in a selenium cell for a definite flux of light energy is very much greater than in the alkali cells even when the illumination is fluctuating rapidly. This, at any rate, has been my invariable experience. Consequently, for equal amplifications, the selenium cell must remain superior in this respect. But when we come to the question of how many valves, or stages of amplification, will be needed to produce a given output of energy, the case becomes different, owing, apparently, to the fact that the "dark resistance" of the alkali cell is practically infinite, while that of the selenium cell as at present available is relatively small. With the alkali cell the connexion to the valve is made between the *grid* and *anode*, and the resulting amplification is, I believe, of the order of 10,000, or possibly more. If we try similar connexions with a selenium cell we find that its comparatively low resistance causes the grid potential to rise so much as to give the saturation anode current even when the cell is dark. The further changes of potential arising from the illumination of the cell are therefore rendered ineffective. This compels one to use the selenium cell in the usual way, namely, to make the current fluctuations operative on the *filament* and *grid* of the valve by transformer or, better, resistance-capacity coupling. An amplification of only about 10 is obtainable in this arrangement.

Thus the alkali cell secures an advantage of 1000 times in the first stage of amplification, so that, although the total amplification required by the selenium cell is *less*, the actual number of valves required in cascade may possibly be *more* than for the alkali cell.

This, of course, arises somewhat fortuitously from the fact that wireless valves commonly obtainable happened to be more adaptable to alkali cells than selenium cells. It ought to be possible to construct a special type of valve to work with selenium cells in the same way as standard types are now combined with alkali cells. Given a 10,000 amplification in the first stage, all subsequent stages would ap-

parently be unnecessary with selenium cells; according to the information available it would be more than enough.

Dr N. R. Campbell. What I maintain is that Prof. Thirring's attempt to compare selenium and photo-electric cells on the basis of some "sensitivity" common to both is unscientific. The nature of the two devices is so dissimilar that, if they are to be compared for some particular use, the comparison must be made on the basis of the results actually attained, and not on the basis of what would be obtained *if* other things were equal, for actually they are not equal.

Prof. F. A. Lindemann. As to the question of the sensitivity of different types of cell, this is largely a matter of definition. If one defines it as a change in resistance per unit light one can obviously prove that the alkali metal cells are much more sensitive than any others, since the effective resistance may be made to vary by an enormous number of ohms per lumen of incident energy. Conversely, if one defines it as a variation in current per lumen, Dr Thirring may justifiably claim that he obtains a greater variation in amperes per unit incident light than any other cell. This, however, is not the point at issue. How absurd a result can be obtained by these arbitrary definitions may be illustrated by considering the ratio of the incident energy to the energy ultimately released. One erg falling upon a square centimetre of a photographic plate will cause a developable image. If one places this plate in the path of a beam of light one can produce an effect as large as one likes either by using a strong beam or by waiting long enough. Thus one erg of incident radiation gives rise to as many ergs as one pleases in the result. Yet nobody would claim, because by using a photographic plate one can release quantities of energy incomparably greater than the incident energy, that the photographic plate is a photoelectric device preferable to a photo-electric cell. The question is, which device gives quick response to small fluctuations of light in such a form that high amplification can be employed and to this question it seems to me there can only be one answer. In this respect I have yet to test the photo-electric device which can compare with the alkali photo-electric cell.

Prof. H. Thirring. I may point out in the first instance that distortion and compensation are quite familiar processes in almost every branch of electric transmission of sounds. Of course, it would not be wise to introduce unnecessary complications in the sound film apparatus unless certain advantages would ensue from the employment of selenium cells. In our case the advantage lies in the greater energy output given from the selenium cell which makes a smaller amount of amplification necessary. It has been argued certainly that alkali cells may be used with only a two-stage amplifier giving sufficient sound volume. Still this proves only that modern valves may afford very large amplification with only two stages, and the fact remains that the currents given by the alkali cells need more amplification than those given by the selenium cells. The drawback of a large amplification lies—quite independently of the number of stages—in the fact that all disturbing noises caused by electromagnetic induction are likewise more enhanced, or, as has been pointed out in my paper, the output of the alkali cells lies nearer to the general disturbance level than that of the selenium cell.

Prof. F. A. Lindemann. I am afraid there is little prospect of my agreeing with

Dr Thirring about the usefulness of the selenium cells. Whilst they can be used for trigger action effects, I cannot agree that they are to be recommended for accurate reproduction of varying light in the form of fluctuating electric currents. The current produced is not proportional to the light—a grave disadvantage in itself. Again, the rate at which the current builds up is comparatively slow, so that for the amounts of light at present employed high frequencies give a much smaller response than low frequencies. If one endeavours to correct by amplifying the high frequencies more than the low frequencies one may be able to achieve for a given amount of light a more or less recognisable reproduction, but if this has been balanced for one amount of light it will not suit a different amount of light; in other words, if the high notes are recognisable with high intensities they would disappear at low intensities, or, inversely, if they can be heard at low intensities they would be grossly exaggerated at high intensities. I must confess that the method of justifying a cell which distorts, by saying one can correct it by distortion in the amplifier, does not commend itself to me. It is as though a politician were to justify himself for giving a distorted version of an event by saying that the opposition newspapers would no doubt distort his speech sufficiently to enable the public to form some true conception of what had happened.

Dr F. C. Toy. I do not feel sufficiently expert to discuss the relative merits of selenium and photo-electric cells, but as we have used both kinds at the British Photographic Research Association there are one or two observations I would like to make. I think the selenium cell, if properly used, is a much better instrument than it is sometimes made out to be. Of course a great deal depends on the way it is used. We use one of the type designed by Prof. Thirring in a form of density meter for the measurement of the density of photographic negatives. The optical arrangement is such that the cell is always exposed to constant illumination, so that although the opacities to be measured may vary from 1 to 10,000 the illumination on the cell is the same. This is done by an arrangement whereby the light reaching the cell is that which has passed through an opacity equal to the highest opacity that can be measured by the machine. This total constant opacity is made up partly by that to be measured and partly by a neutral grey wedge, the amount of the latter in the beam being decreased as the former increases. In this way the "lag" of the cell (which is a serious drawback if changes of intensity from 1 to 10,000 occur on the cell face) is reduced to a time scarcely any longer than that necessary for making the wedge adjustments.

Another point, on which I should like some information, is the spectral sensitivity of selenium cells. I feel very doubtful if they are equally sensitive (for equal incident energy) over the whole visible spectrum as has, I believe, been suggested.

In our large and more accurate density meter we use a potassium hydride photo-electric cell which has, I think, one special feature which may be of interest. Instead of having a single window, as is the usual practice, there are two windows at right angles to one another. The result of this is that the two beams of light (one through the unknown opacity and one through a neutral wedge) can be arranged symmetrically in relation to the light source and yet each beam be only turned

through one right angle instead of 2 or 3 as in some photometers. The result is a considerable simplification of the optical system.

In using these photometers for the measurement of photographic negatives it is necessary to cover the window of the cell with some good diffusing medium such as opal glass.

Mr L. V. Chilton. Dr F. C. Toy has referred to the occasional necessity, when using the photo-electric cell in measuring the densities of photographic negatives, of covering the cell window with a diffusing medium such as opal glass. In view of this fact, which incidentally overcomes the trouble due to local irregularities in the photo-electric sensitivity of the cathode surface, it would be interesting to know whether manufacturers of photo-electric cells ever employ diffuse light in standardising them. It seems likely, moreover, that as the use of a diffusing window would cut down the maximum intensity of light striking the cathode surface and therefore the photo-electric current *density* over the latter, we might expect the life of the cell to be prolonged thereby. I should like to know also whether there would be any objection, other than loss of light, to the use of such a diffusing window in sound-film practice, as it would provide the same advantage of rendering unimportant local variations of photo-sensitivity of the cathode surface.

Major C. E. S. Phillips. I should like to point out that the sensitivity of selenium cells for various wave-lengths of light may be widely varied by heat treatment.

Dr T. H. Harrison. The colour sensitivity of selenium cells is a function of the intensity of the illumination falling upon the cell. The alkali metal photo-electric cells, on the other hand, unless used too near the glow voltage, possess a colour sensitivity which is independent of the intensity of illumination. The dependence of the colour sensitivity of the selenium cell upon the intensity of illumination is an unfavourable feature which renders the selenium cell useless for most forms of photometry and cannot fail to have a somewhat harmful effect in its use for sound reproduction.

Prof. F. A. Lindemann. I am interested to learn that the selenium prepared by Dr Thirring is not sensitive far into the infra-red. It is sometimes forgotten that it is a definite disadvantage to use photo-electric cells whose sensitivity extends too far beyond the visible. The fraction of energy falling upon a cell from the ordinary temperature radiation at wave-lengths within an octave or two of the visible region is by no means negligible compared with the amount of incident energy usually employed and it is essential when regularity of working is necessary that the cell should only be affected by the radiation which is deliberately used in order to produce a current. We have always borne this fact in mind and perhaps in consequence we have never been troubled with so-called dark currents.

Dr L. Simons. The fissures of retreat that appears in the photo-micrographs of films shown by Major Phillips in connexion with his paper recall to my mind some early experiments of Prof. H. A. Wilson on the stability of gold leaf. He showed that this depended upon the relative values of the opposing effects of surface tension and viscosity and that a temperature could be arrived at when the effect of surface tension was the greater and the film crumpled. If the film were mounted this would

mean a breakdown. The continuity of film structure has recently acquired a new importance in many physical applications. In two cases I have noticed the complete breakdown of sputtered gold film on celluloid, the mirror-like transparent blue film becoming granular and microcrystalline in appearance under a high power. In each case the film had been exposed to X-rays, the presumed action of which is to produce intense local hot spots. The nature and the previous treatment of the surface immediately underlying the film must have an important bearing on its stability.

Mr G. P. BARNARD (communicated). Major Phillips' observations on the effect of oil in reducing the remanence and inertia effects and in increasing the dark resistance of selenium cells are extremely interesting. I should like to know whether he has any explanation to offer for this effect. The viscosity of selenium in the molten state hinders crystallisation and favours solidification in the form of a heterogeneous assemblage of molecules; the mutual relations of the molecules in that state are stereotyped at the moment of cooling. It seems possible, therefore, that the effect of oil is to increase the mobility of the surface molecules of the mass, which does not then possess the freedom of the liquid state, so as to permit their aggregation, under the influence of the forces of surface tension, into characteristic forms. His observations appear to emphasise the fact that the form and structure of layers and films of selenium are primarily controlled by the forces of surface tension and cohesion, so that the state of aggregation is dependent on the medium (liquid or gaseous) in which the layer or film is produced, assuming that no chemical action takes place at the surface of the layer.

In connexion with the author's remarks on the production of films by sputtering, it is interesting to note that Kahler has found that microscopic examination of such films has revealed them to be of a very spongy nature, giving the appearance of irregular mechanical treatment.

I am very dubious concerning the fulfilment of the hope expressed in the last paragraph of the paper. The selenium layer in a cell may be regarded as a viscous electrolyte. Its heterogeneous nature conceals the primary production of electrons by the light according to the quantum equivalent equations. These electrons are caught or slowed down by all kinds of cracks, irregularities, or impurities; in fact, if these are sufficiently numerous, the primary photo-current disappears altogether. What is mainly observed in commercial selenium cells is a secondary current, electrolytic in nature, following the primary ionisation. The secondary effect is due to a general loosening of the crystal structure owing to the accumulation of charges inside the crystal. The fact that a deposit of amorphous selenium occurs on the anode of the cell through which a direct current passes is well known and has been stated to be the cause of the secular deterioration of cells. Benson describes a process of re-sensitisation of cells by the use of alternating currents.

The complications involved owing to the heterogeneity of the crystal mass render it impossible to provide any quantitative explanation of the light-sensitivity of these cells. If precautions are taken to avoid the secondary phenomena due to the accumulation of charges, as Gudden and Pohl have done in their experiments on red, crystalline selenium, it is found that the primary photo-currents are only of

the order of 10^{-12} ampere; but they are inertialess and, further, strictly proportional to the absorbed light-energy. The use of the primary photo-currents would, however, involve the development of a new type of "selenium cell," and a distinct departure from the methods of cell-construction now in use.

Major C. E. S. PHILLIPS (communicated). In reply to Mr Barnard, it appears that oil increases the resistance of the cells by penetration of the porous crystalline mass. Since a potential gradient of 2000 volts per cm. is not unusual in selenium cells, considerable electrostatic forces have to be reckoned with. I have frequently noticed that with oil and a high potential gradient there is a momentary current of about 200 microamperes on first completing the circuit, which rapidly falls to about 5 microamperes. Such a cell is practically without lag. The explanation is difficult to arrive at, but I suggest that the effect points to a suddenly increased cohesion of the mass and the squeezing out of the oil, to be followed by a release to a condition of equilibrium. More experimental results are required upon this and numerous other aspects of the problem of the light-sensitive properties of selenium.

Prof. H. THIRRING. Can anyone give me data concerning the working efficiency of the modern gas-filled alkali cell, that is to say, the ratio of their actual sensitivity to the theoretical maximum of sensitivity? The maximum would be reached when every incident light quantum whose energy $h\nu$ is greater than the work function of the metal surface is absorbed by releasing an electron. In the case of photographic plates it has been computed, for instance, that the actual sensitivity is less than 1/1000 of the theoretical maximum.

Prof. F. A. LINDEMANN. The efficiency of gas-filled photo-electric cells is of the order of magnitude of one in a thousand.

Mr J. A. MORROW. I should like to know if there is any reason to expect a photo-electric cell to respond to any special way to radiations from incandescent metal (vapour) of which its own cathode is composed.

Dr N. R. CAMPBELL. The variations of emission over a single cathode do not follow at all closely the variations in optical properties, indicated by the general appearance. Parts of entirely different appearance may have the same emission and—less frequently—those with the same appearance may have different emissions.

Prof. F. A. LINDEMANN. Much time has been spent in discussing difficulties and troubles found by various physicists which are due to causes that are quite avoidable and in every sense of the word secondary. We have never had any such difficulties whether they arise from gradual leakage of charge over the insulating parts of the cell or from the change in the sensitivity of the cells with time, or even from the variation between different cells made in the same way. In making cells we have always taken precautions to avoid these difficulties, and I think I may claim that amongst the thousands of cells made by us only a small proportion fail by more than 10 per cent. to achieve the uniform standard at which we aim.

At this meeting we have scarcely discussed the interesting theoretical aspects about which so little is at present known. One of these questions is the possibility of increasing the wave-length at which the maximum sensitivity of the cell occurs. For the reasons I gave yesterday I do not consider this to be desirable for cells used in technical practice, but theoretically it is of the utmost importance. It would

seem that the electron can only be detached from the metal with a longer wave-length by using the field of a neighbouring atom to diminish the potential against which the electron has to escape. If this is so, the atom assisting the electron must turn or move as the electron escapes and it can only be restored to its original position by adding energy to the system. In this case a photo-electric cell sensitive at long wave-lengths must either gradually lose its sensitive qualities or the juxta-position of the atoms must be re-established. In other words, if such a cell is to continue to act uniformly, some form of time-lag or fatigue would appear to be inevitable.

Very little again has been said about the selective and the normal photo-electric effects. That two phenomena so different, one depending upon polarisation with a well-marked band of maximum sensitivity, the other apparently similar in type in all metals and independent of the angle of incidence, should be due to the same, or even similar, mechanism seems highly improbable. That the colour of the hydride is not the determining factor was shown long ago by Pohl who measured the electron emission per unit of absorbed energy. Work on these subjects is difficult, partly because we have to rely upon a thermo-element to establish the amount of incident radiation. I am inclined to think we can trust this instrument provided we know its reflection coefficient, since the absorbed energy can only be converted into heat, unless indeed our thermal element produces photo-electrons—a consummation unfortunately extremely improbable. I imagine that we shall have to use photo-electric sub-standards calibrated with black bodies against thermopiles in order to have convenient means of checking the distribution of energy in the ultra-violet. It was in this way that Mr Jeffrees standardised the instruments made for us by Messrs Bellingham and Stanley for use by medical men who are examining the therapeutic effect of light. The method, is, of course, troublesome and not very accurate, but it seems difficult to obtain anything very much better. Scientific work requires some method of measuring the incident radiation before one can discuss seriously the theory of photo-electric phenomena which underlie all those practical applications of which we have heard so much.

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PHOTO-ELECTRIC CELLS AND THEIR APPLICATION — ANDERSON